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54 Acryl functional slllcone compounds.

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| 56 References cited: DE-A- 3 006 167 | Midland Michigan(US) |
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EP 0 230 342 B1

EP 0 230 342 B1

divalent hydrocarbon radicals bonding at least two silicon atoms together, and silicon atoms which are present and which do not have an acryl functional radical bonded thereto can have any of the other groups bonded to them as stated herein.

The acryl functional silicon compounds of this invention can be prepared by intimately mixing an amino functional silicon compound having at least one primary amine or secondary amine group with an acryl functional compound having at least two acrylate, methacrylate, acrylamide, or methacrylamide groups per molecule. For purposes of this invention, the term "acryl functional" or "acryl functionality" refers to the following groups: acrylate ($\text{CH}_2=\text{CHCOOC}-$), methacrylate [$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}-$], acrylamide [$\text{CH}_2=\text{CHCONHC}-$], and methacrylamide [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CONHC}-$]. When amine compound and acryl compound are mixed, there is a reaction which produces an acryl functional silicon compound. This reaction is known as the Michael-type addition reaction. This reaction occurs at room temperature but is rather slow for many commercial applications, for example, the reaction may take as long as 24 hours or more to convert only 40% of the amine to the acryl functionality.

Heating the mixture increases the rate of the reaction and at 70°C as much as 80% of the amine can be converted to the acryl functionality. The mixture should not be heated above 100°C because temperatures above 100°C can cause considerable loss of the acryl functionality due to a free radical initiated chain reaction. Free radical scavengers, such as p-methoxyphenol, are useful to inhibit the unwanted chain reaction, but these scavengers also inhibit the reactivity of the final acryl functional silicone compound during its use unless they are removed. Although free radical scavengers can be used, their use would add expense to making improved purity acryl functional silicone compounds.

If the intimate mixture is formed in a solvent, the reaction rate may increase slightly, such as in a 24 hour period at room temperature up to 45 to 50% of the amine may be converted to the acryl functionality. Solvents referred to are those which are commonly used for silicone reactions such as toluene, xylene, benzene, hexane, pentane, mineral spirits, trimethylsiloxy endblocked polydimethylsiloxane, and cyclopolydimethylsiloxane. Many of these solvents have high boiling points, are difficult to remove from the acryl functional silicone compounds produced, have environmentally undesirable properties, and are hazardous to use. Thus, besides providing low conversion, these solvents have other undesirable properties.

The best reaction conditions are those in which the intimate mixture is formed using a promoter solvent, such as an alcohol. The preferred alcohols are those which can readily be removed from the reaction product without having to heat it to too high of a temperature. Examples of promoter alcohols are ethanol and isopropanol. The use of the promoter solvent can increase the rate of the reaction such that 90 to 95% of the amine is converted to the acryl functionality. The fastest reactions would be those using a promoter solvent and heating the mixture to a temperature above 25°C and below 100°C .

Any of the above reactions can be used to make the acryl functional silicone compounds of this invention. Although some of the methods use solvents, the resulting products are purer than those reactions which use amines to form salts of the by-produced acid. These methods offer the advantage that the silicone compound can be prepared in the desired structural form before the acryl functionality is in place on the molecule. The amine functional silicon compounds can withstand the higher temperatures of preparation while the acryl functionality cannot. For example, the preparation of poly(co-diphenylsiloxane-co-dimethylsiloxane) requires an alkaline equilibration catalyst with heating to high temperatures, such as 150°C , of a mixture of cyclopolydimethylsiloxane and cyclopolydiphenylsiloxane. The preparation of a polymer having dimethylsiloxane units, diphenylsiloxane units, and siloxane units having acryl functionality could not survive the reaction without causing the acryl functionality to polymerize and thus an acryl functional silicone compound of this type could not be produced. However, the method of this invention can be used to prepare such compounds. For example, the mixture of the cyclopolydimethylsiloxane, the cyclopolydiphenylsiloxane, the alkaline equilibration catalyst, and an amine bearing siloxane precursor could be used to make an amine functional poly(co-diphenylsiloxane-co-dimethylsiloxane) which could then be converted into an acryl functional siloxane compound at lower temperatures by the method of this invention. The amine functionality can survive such reactions much more readily than the acryl functionality. The amine functionality can survive even more severe conditions, therefore, the method of this invention is an attractive route to acryl functional silicone compounds.

The amine functionality can be either primary or secondary. The primary amine functionality reacts much more readily than the secondary amine functionality. For this reason, the multi-functional acryl compounds used to react with the amine react readily with primary amine and the additional acryl functional groups do not readily react. Such a difference in reaction rates between the primary and secondary amines can be used to advantage in the method of this invention. After one of the acryl groups of the multi-functional compound reacts with the primary amine, the reaction can be stopped by adding monofunctional acryl compounds to react with the remaining secondary amine hydrogens. This method can be used to

EP 0 230 342 B1

prepare acryl functional silicone compounds which have larger amounts of acryl groups but retain shelf stability and also can be used to make compounds which have a desired amount of acryl groups.

The reaction between the amine functional silicon compound and the multi-functional acryl compound can be stopped by adding a monofunctional acryl compound to the reaction mixture. The monofunctional acryl compound can be added at two points during the reaction. The amine functional silicon compound and the multi-functional acryl compound can be mixed and at the point one wishes the reaction stopped, the monofunctional acryl compound is added. One could also add the monofunctional acryl compound at the beginning of the reaction, but this uses up amine hydrogen atoms, especially primary amine hydrogen atoms. The monofunctional acryl compound is preferably added after the reaction has begun so that the monofunctional acryl compounds do not compete with the multi-functional acryl compounds in such a manner that the number of acryl groups on the final silicon compound is not the desired product.

The reaction can also be stopped by another method in which the reaction between the multi-functional acryl compound and the amine functional silicon compound is stopped by adding an acid anhydride. Using the acid anhydride to stop the reaction, has the same benefits as using a monofunctional acryl compound with respects to shelf stability, but the use of the acid anhydride has the added advantage that a new compound is formed, namely one in which the acryl functional silicone compound has the following group



wherein R^7 is a monovalent hydrocarbon radical or a radical of the general formula $-\text{R}^8\text{COOH}$ in which R^8 is a divalent hydrocarbon radical.

The amounts of amine functional silicon compound and the acryl functional compound should be such that there is at least one molecule of acryl functional compound per primary amine hydrogen. It should be understood that the amounts of the amine functional silicon compound and the acryl functional compound can be such that there is less than one molecule of acryl functional compound per primary amine hydrogen, but in such instances precautions should be taken to ensure adequate shelf life for the reaction product. The acryl functional silicone compounds made with less than one molecule of acryl functional compound per primary amine hydrogen may contain crosslinking as a result of two or more of the acryl functional groups on one acryl functional compound reacting with primary amine hydrogen atoms on different amine functional silicone compounds. When two acryl functional groups on one molecule react with two hydrogen atoms of primary amine, groups on different amine functional silicon compounds, the product can gel before it is put to use. The foregoing ratio of acryl functional compound to primary amine hydrogen does not mean that the secondary amine hydrogen atoms do not react but only that they react slower and can be readily stopped from reacting by the above mentioned methods.

The amine functional silicon compounds used in the method of this invention can be any of those known in the art which have primary and secondary amine functionality. These compounds can be prepared by methods well-known in the art and many are commercially available.

Amine functional silanes can be exemplified by the following general formula



wherein R is a divalent hydrocarbon radical or a divalent hydrocarbon radical having amino functionality of the formula $=\text{NH}$ in which the two bonds of the $=\text{NH}$ are bonded to carbon atoms,

R^1 is hydrogen or an alkyl radical having from 1 to 4 carbon atoms per radical, such as methyl, ethyl, propyl, isopropyl, butyl, and isobutyl,

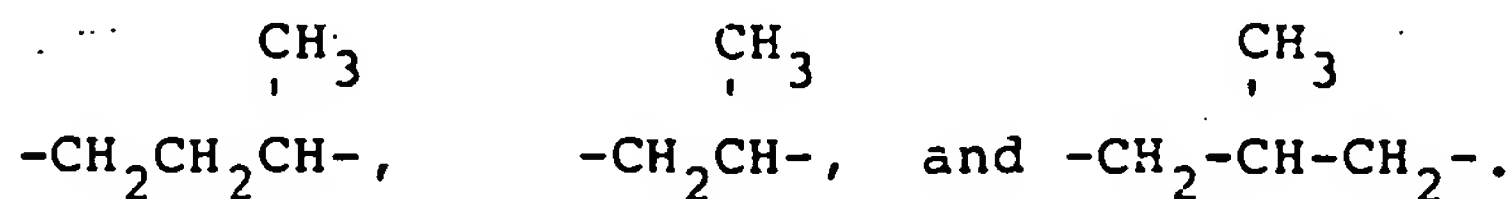
R^2 is a monovalent hydrocarbon radical or fluorinated alkyl radical,

X is a hydrolyzable group whose hydrolyzed groups do not form salts with the nitrogen atom, and

a is 1, 2, or 3.

Examples of R are divalent hydrocarbon radicals, such as methylene, ethylene, butylene, hexylene, propylene, decylene,

EP 0 230 342 B1



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R can also be a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, such radicals are illustrated by -CH₂CH₂CH₂-NH-CH₂CH₂-, -CH₂CH₂CH₂-(NH-CH₂CH₂)₂-, -CH₂CH₂CH₂-(NH-CH₂CH₂)₃-, and -CH₂CH₂CH₂-(NH-CH₂CH₂)₄-.

10 R² can be illustrated by methyl, ethyl, propyl, butyl, phenyl, octadecyl, 2-phenylethyl, vinyl, 3,3,3-trifluoropropyl, 2-(perfluoroethyl)ethyl and 2-(perfluorobutyl)ethyl. X is illustrated by an alkoxy radical or an N,N-dialkylamino radical. Examples of alkoxy radical are methoxy, ethoxy, propoxy, butoxy, 2-ethylhexoxy, isopropoxy, hexyloxy, 2-methoxyethoxy, 2-ethoxyethoxy. Examples of N,N-dialkylamino radicals are dimethylamino, diethylamino and diisopropylamino. Examples of such silanes are gamma-aminopropyl-

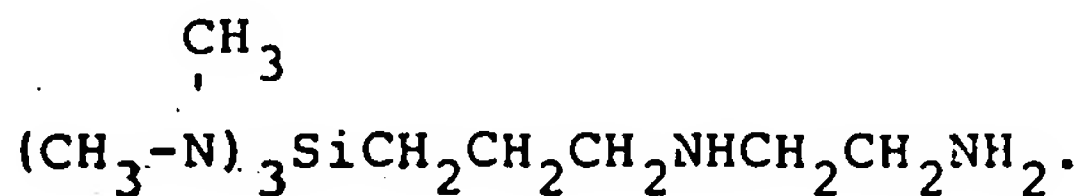
15 triethoxysilane, gamma-aminopropylmethyldiethoxysilane, gamma-aminopropylethyldiethoxysilane, gamma-aminopropylphenyldiethoxysilane, delta-aminobutyltriethoxysilane, delta-aminobutylmethyldiethoxysilane, delta-aminobutylethyldiethoxysilane, delta-aminobutylphenyldiethoxysilane, gamma-aminoisobutylmethyl-

20 dimethoxysilane, aminomethyltrimethoxysilane, gamma-aminopropyltrimethoxysilane, N-methyl-gamma-aminopropyltrimethoxysilane, gamma-aminopropyltripropoxysilane, gamma-aminopropyltri(methoxyethoxy)-

silane, beta-aminoethyltriethoxysilane, gamma-aminobutyltriethoxysilane, N-methyl-gamma-aminopropyl-

25 methyltributoxysilane, delta-aminobutyltrimethoxysilane, delta-aminobutyldimethylmethoxysilane, beta-aminopropyltriethoxysilane, (CH₃O)₃SiCH₂CH₂CH₂NHCH₂CH₂NH₂, (CH₃O)₃SiCH₂CH₂CH₂(NHCH₂CH₂)₂NH₂, (CH₃O)₃SiCH₂CH₂CH₂(NHCH₂CH₂)₃NH₂, (C₂H₅O)₃SiCH₂CH₂CH₂(NHCH₂CH₂)₄NH₂, N-butyl-gamma-aminopropyltrimethoxysilane and N-methyl-beta-aminopropyltriethoxysilane. Example of N,N-dialkylamino silanes are gamma-aminopropyltris(N,N-dimethylamino)silane, gamma-aminopropyltris(N,N-diethylamino)silane, and

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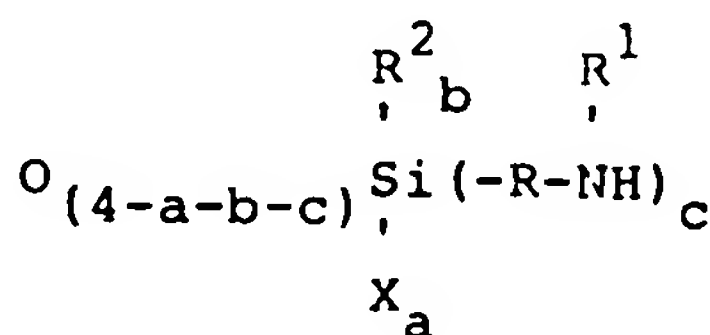


35 The silanes described above can be hydrolyzed in any combination to provide amine functional silicon compounds which can be used in the method of this invention to make acryl functional silicon compounds. These silanes can also be hydrolyzed with other silanes which do not contain amine functionality to make still other amine functional silicon compounds for use in the method of this invention.

The hydrolyzed silanes described above and siloxanes made by equilibrating cyclic siloxanes can make

40 amine functional siloxanes which can be used in the method of this invention to make the acryl functional silicon compounds. These amine functional siloxanes have a general average unit formula

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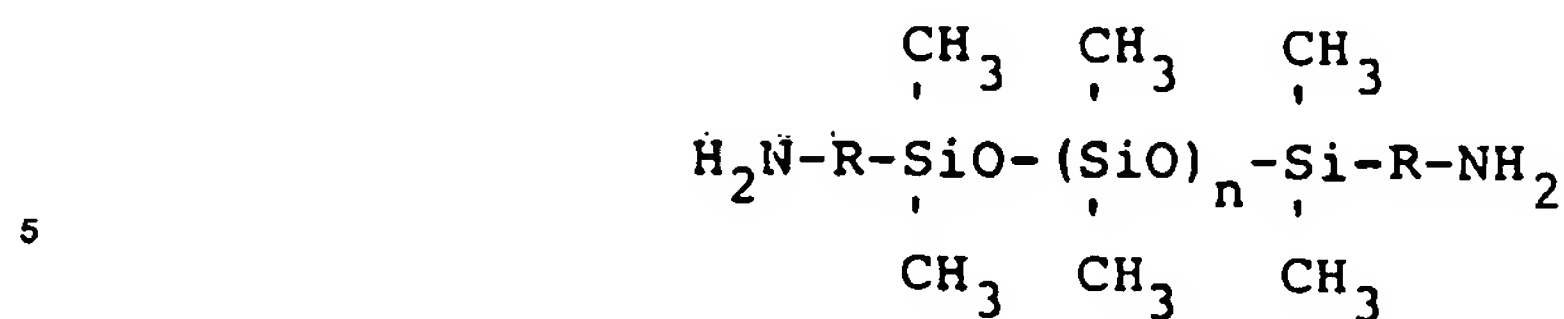
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in which R, R¹, R², and X are the same as defined above, a has an average value of <3, b has an average value of <3, c has an average value such that there is at least one -R-NHR¹ radical per molecule of amine functional siloxane, and the sum of a + b + c is <4.

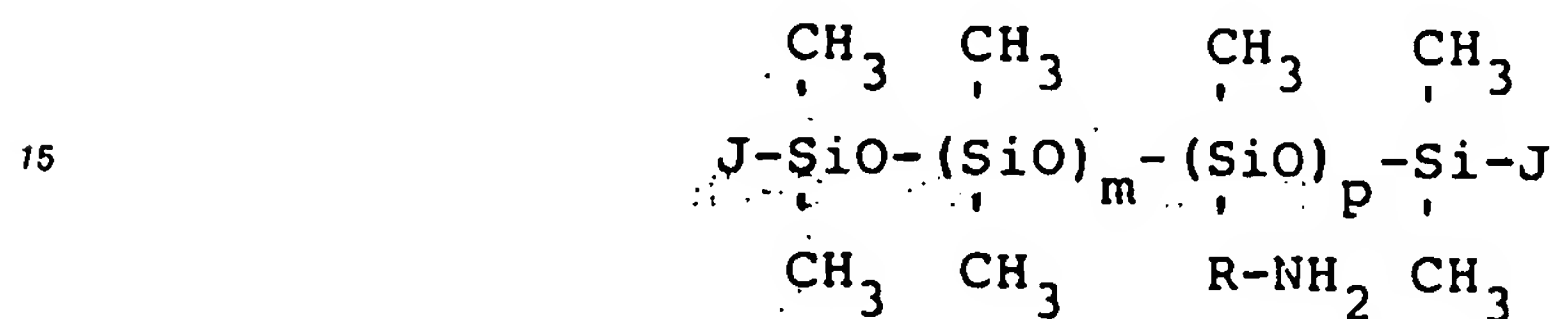
A preferred amine functional siloxane for this invention has the following formula

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EP 0 230 342 B1



10 in which R is defined above and n has an average value of zero or greater, preferably 10 to 300. Other preferred amine functional siloxanes for this invention are those having the following general formula



20 in which R is defined above; J is either methyl or -R-NH₂, preferably methyl; m has an average value of zero or greater, preferably 100 to 500; and p has an average value of at least one, preferably 2 to 20.

The multi-functional acryl compounds used in this invention are available commercially or can be made by well-known methods. Examples of the difunctional acryl compounds are the diacrylates, including

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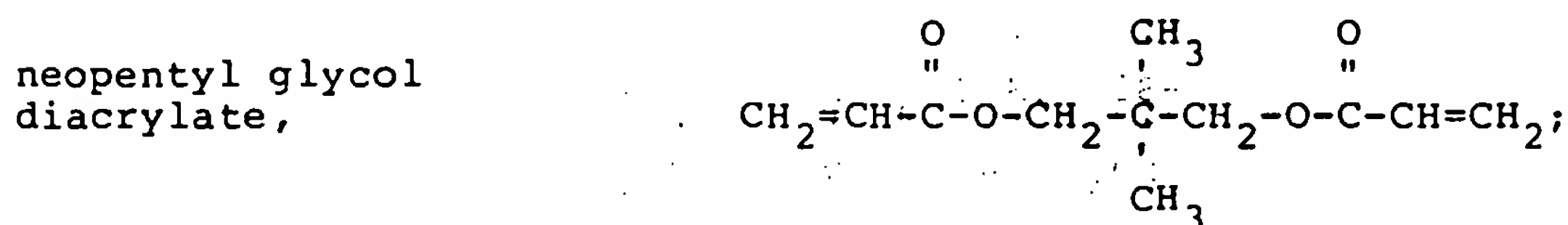
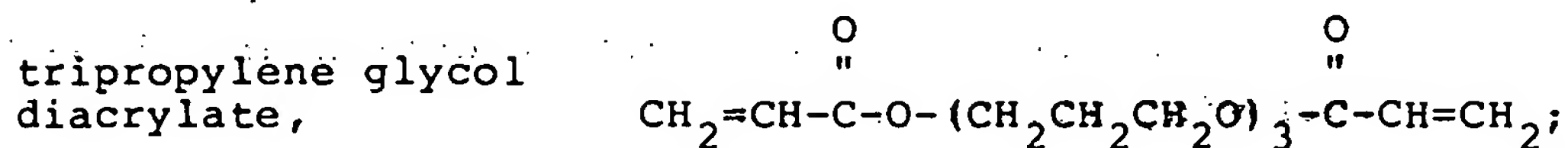
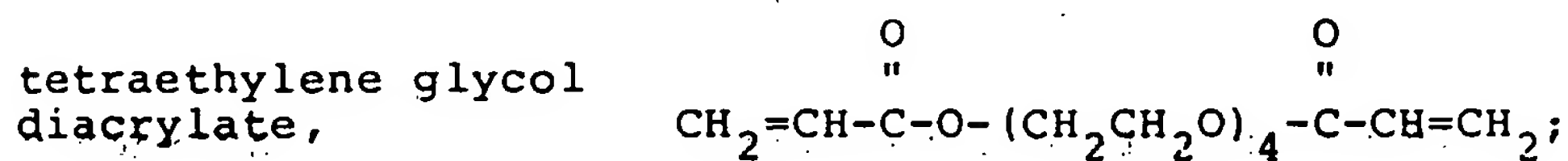
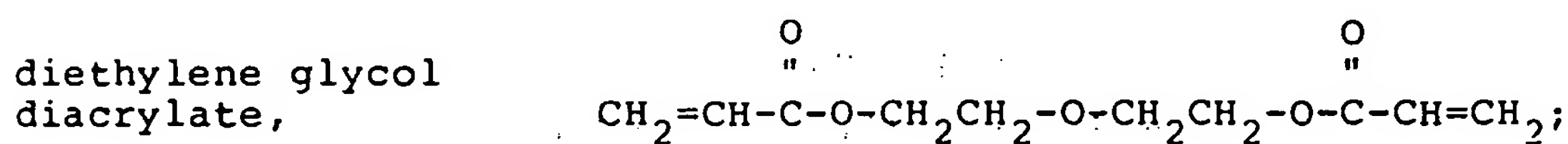
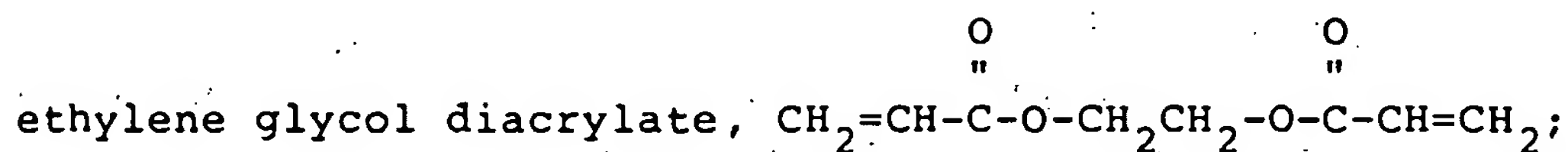
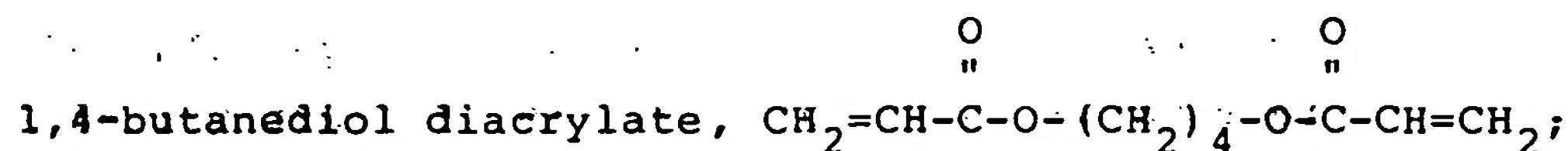
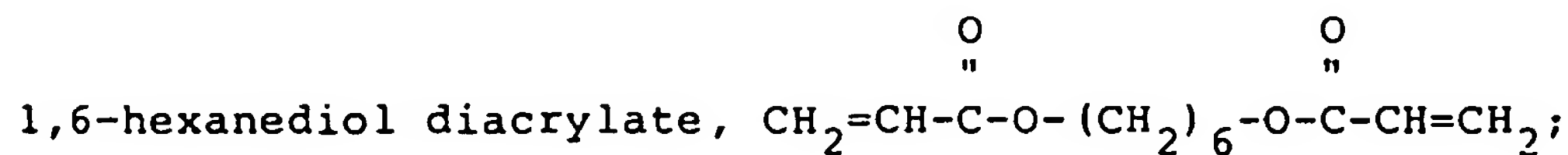
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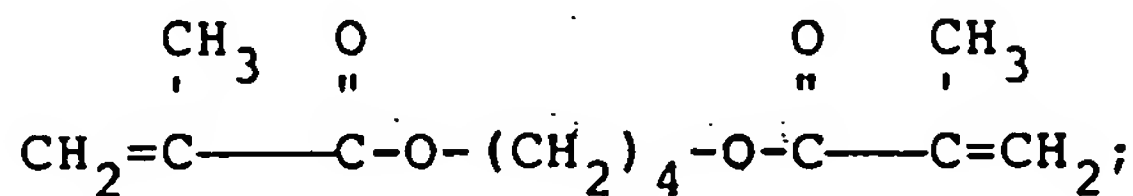
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EP 0 230 342 B1

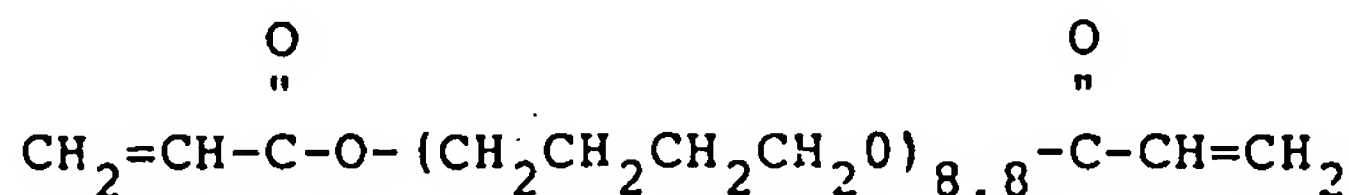


EP 0 230 342 B1

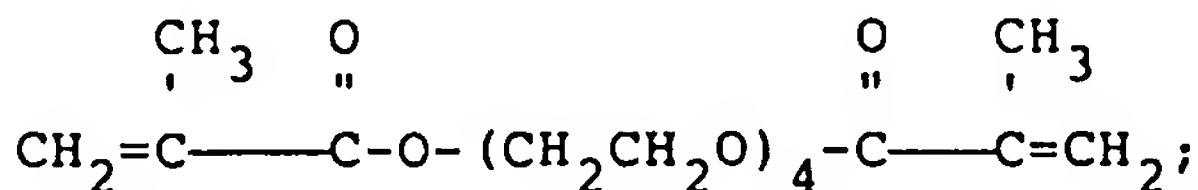
1,4-butanediol
dimethacrylate,



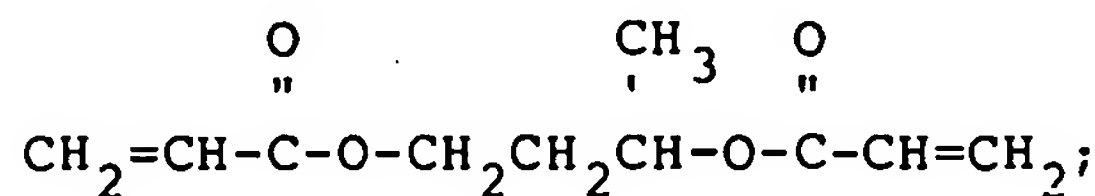
poly(butanediol)
diacrylate,



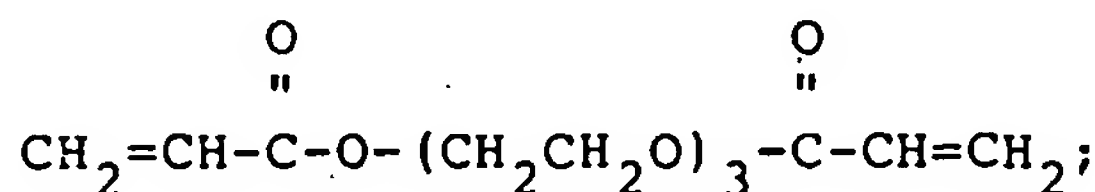
tetrathylene glycol
dimethacrylate,



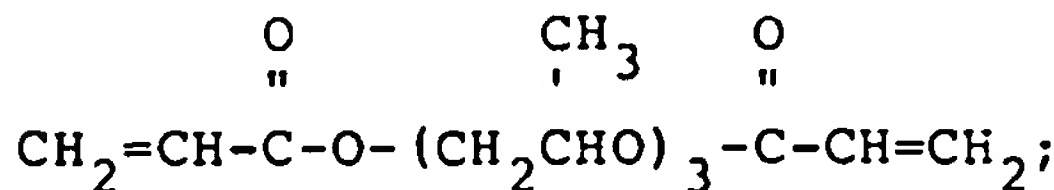
1,3-butylene glycol
diacrylate,



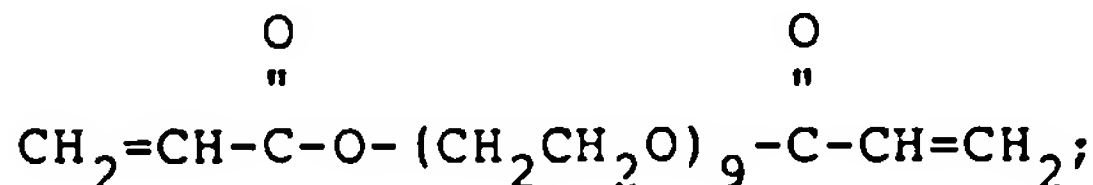
triethylene glycol
diacrylate,



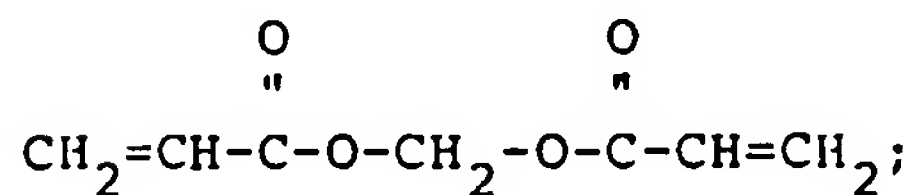
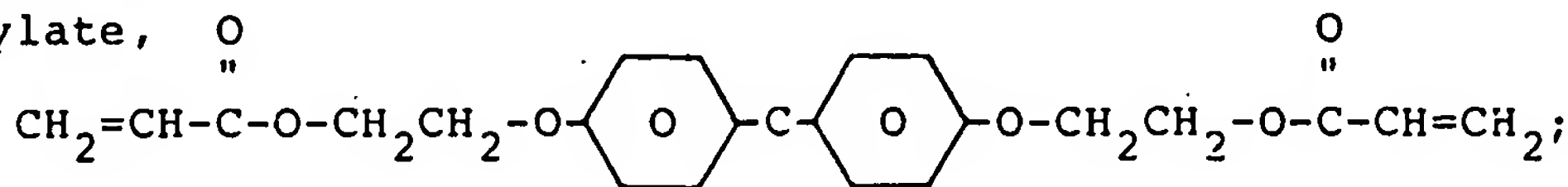
triisopropylene
glycol diacrylate,



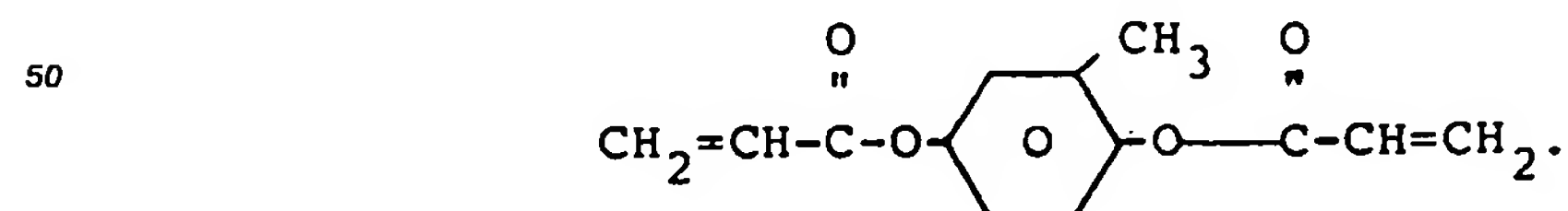
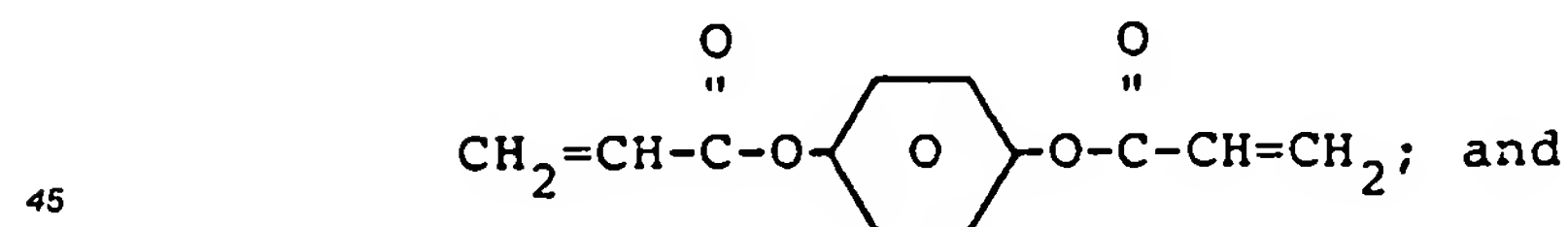
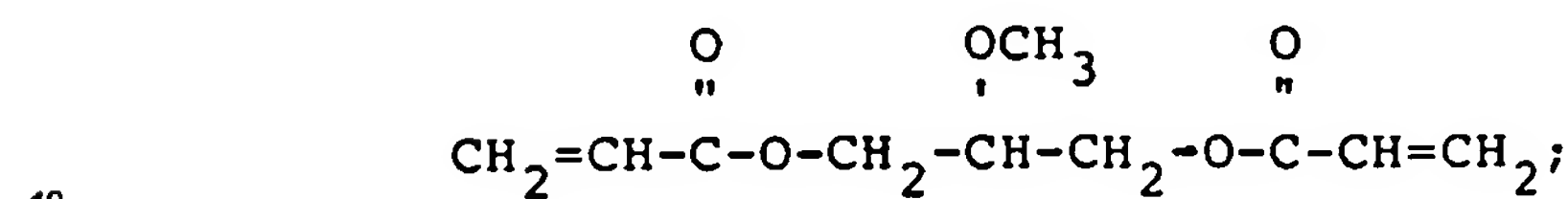
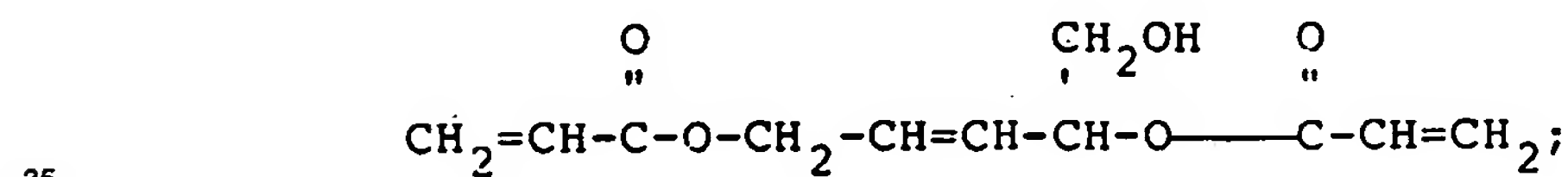
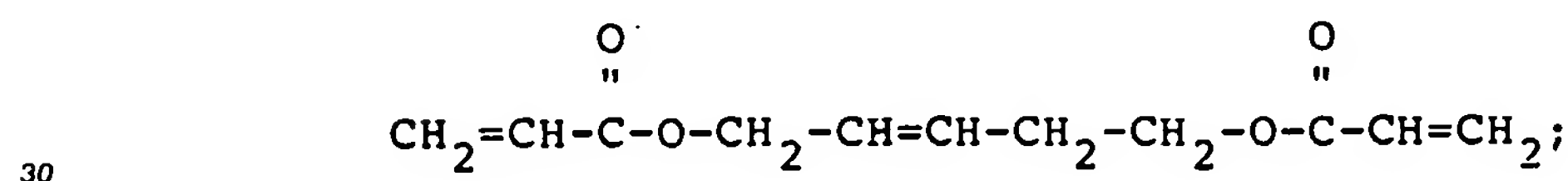
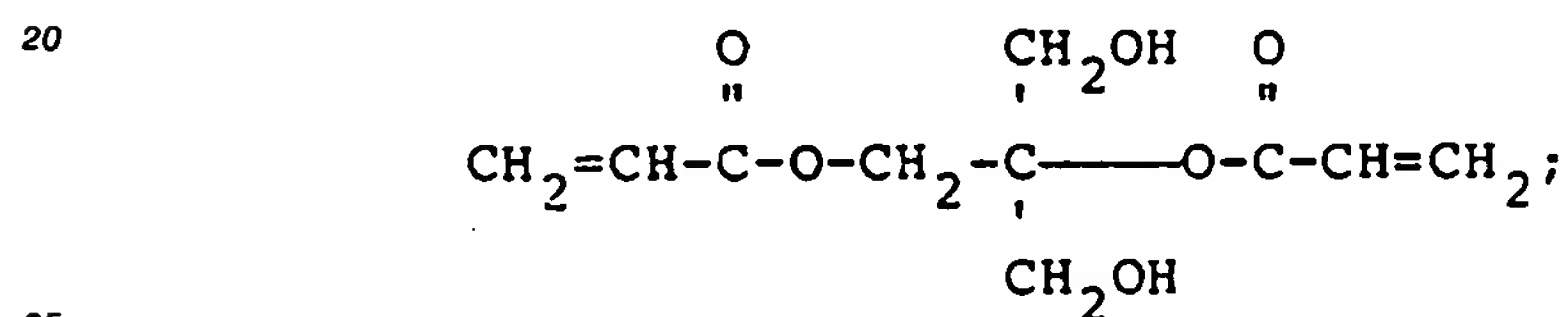
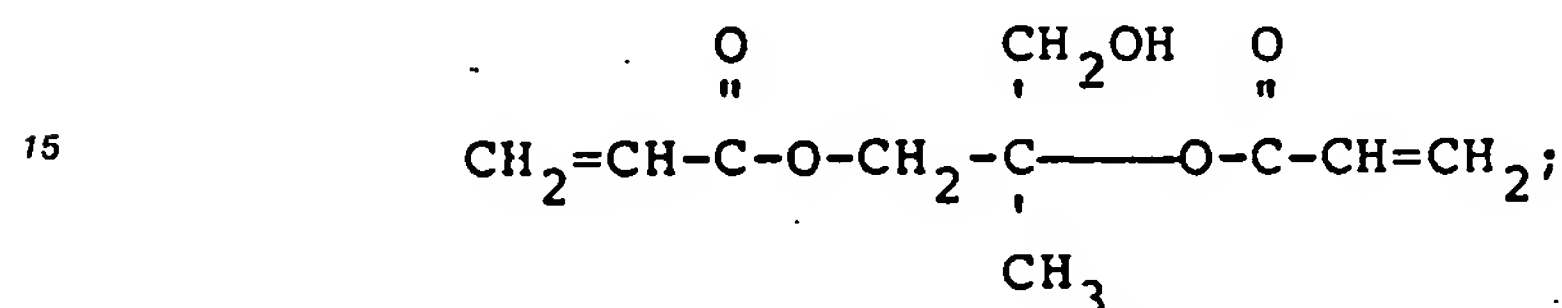
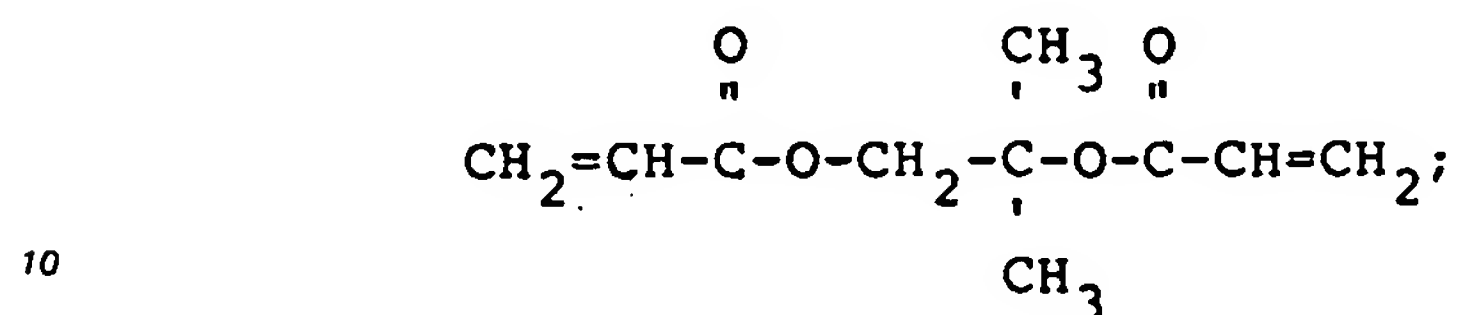
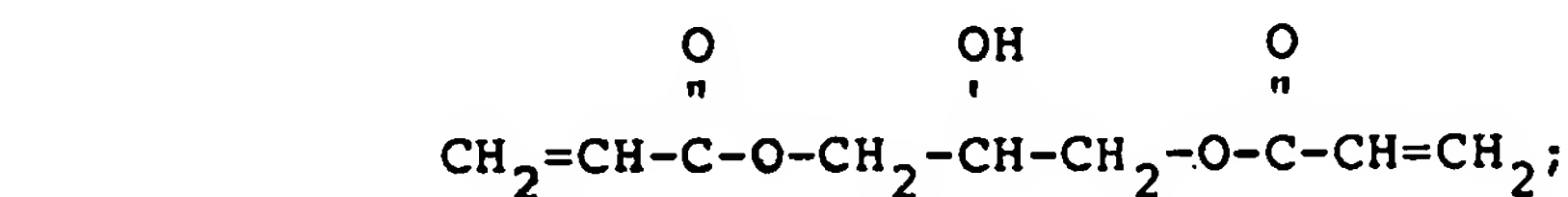
polyethylene glycol
diacrylate,



ethoxylated
bisphenol A
diacrylate,



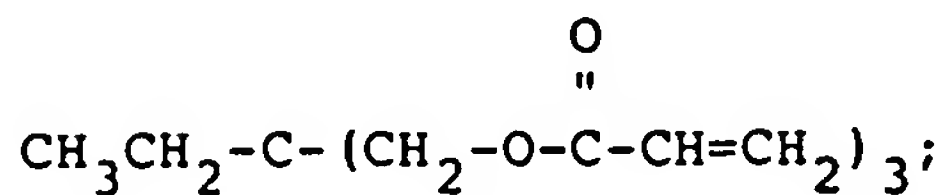
EP 0 230 342 B1



55 Examples of acrylates which have three or more acrylate groups include

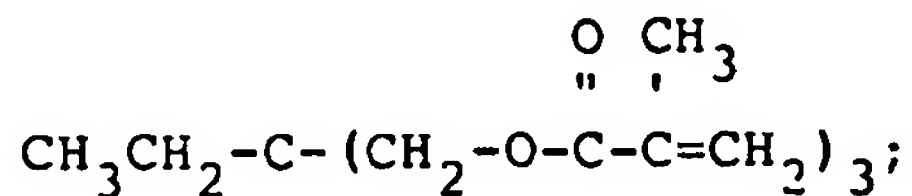
EP 0 230 342 B1

trimethylolpropane
triacylate,



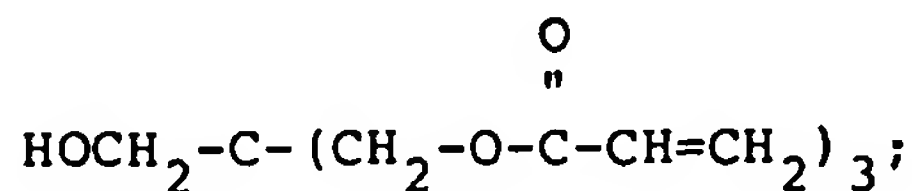
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trimethylolpropane
trimethacrylate,



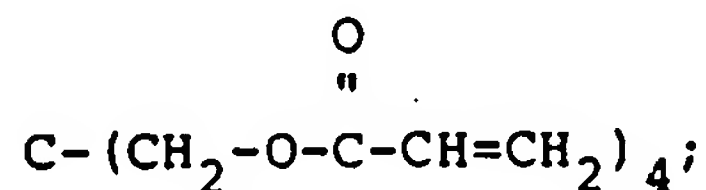
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pentaerythritol
monohydroxy
triacylate,



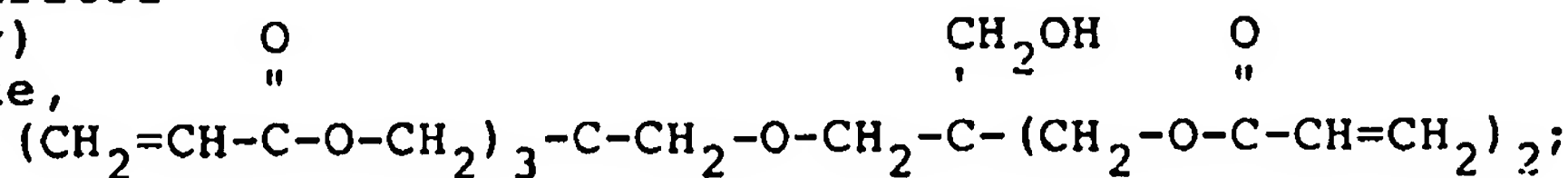
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pentaerythritol
tetraacylate,



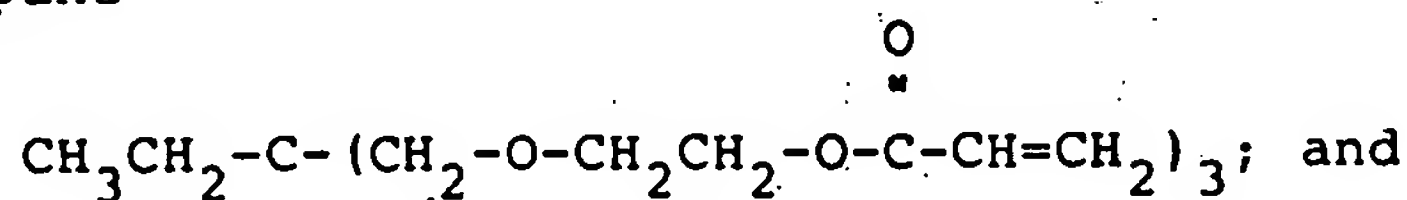
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dipentaerythritol
(monohydroxy)
pentaacylate,



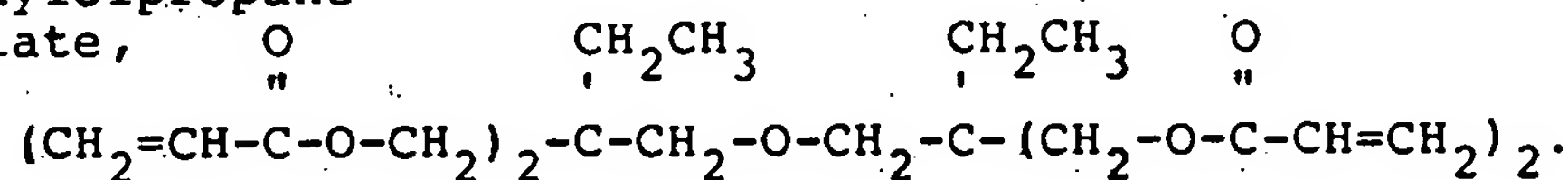
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trimethylolpropane
triethoxy
triacylate,



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di-trimethylolpropane
tetraacylate,



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Examples of acrylamide compounds include

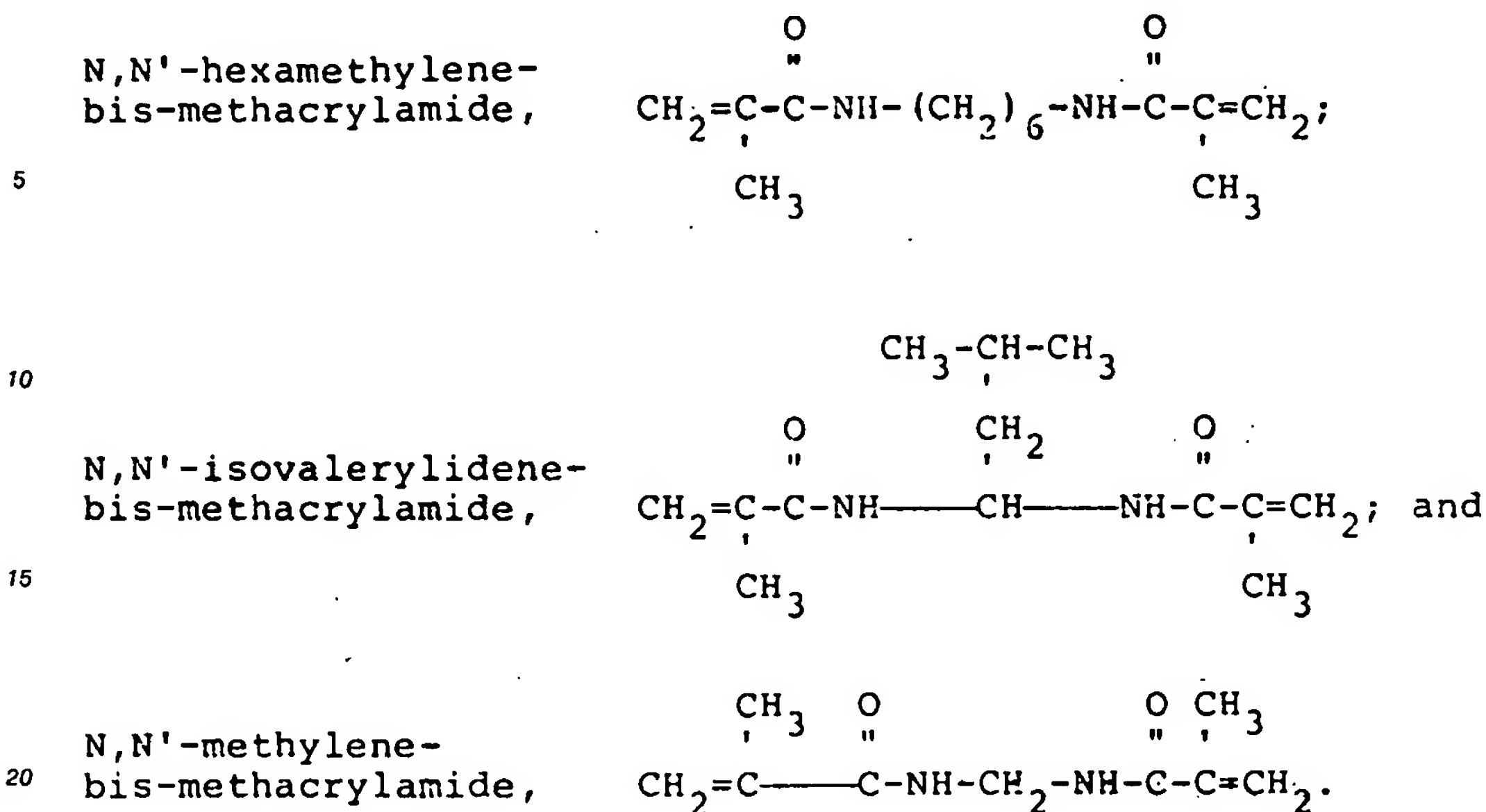
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EP 0 230 342 B1

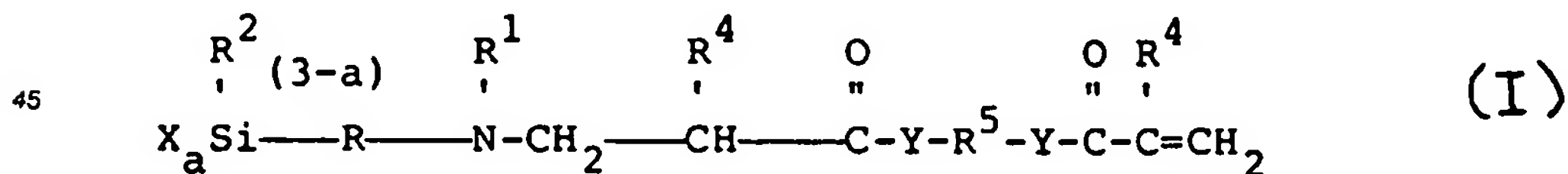


The monofunctional acryl compounds used to stop the reaction between the multi-functional acryl compound and the amine functional silicon compound can be illustrated by ethylhexyl acrylate, isobornyl acrylate, methyl methacrylate, n-butyl acrylate, ethyl acrylate, methyl acrylate, N,N'-dimethyl acrylamide, and ethyl methacrylate.

The anhydrides which can be used to stop the reaction and also produce new compounds can be illustrated by acrylic anhydride, acetic anhydride, propionic anhydride, butyric anhydride, isovaleric anhydride, caproic anhydride, palmitic anhydride, stearic anhydride, succinic anhydride, and glutaric anhydride. Acryl functional silicon compounds which are prepared using the anhydride can exhibit suitable release characteristics for use in making paper coating compositions.

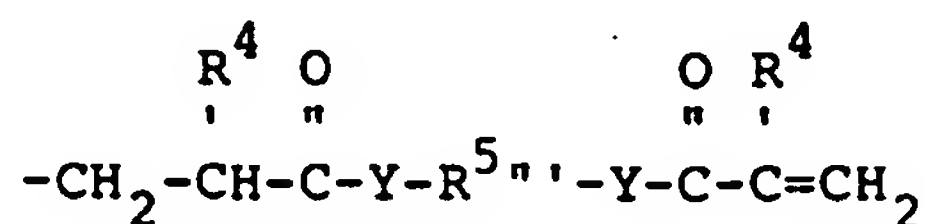
The acryl functional silicon compounds of this invention can be used in many applications from coupling agents, to adhesion promoters, to polymers which can be cured by ultraviolet radiation, to heat curable compositions, to compositions which can be cured by electron beam radiation, as well as other radiation. One of the advantages of the acryl functional silicon compounds of this invention is that the compounds do not need to contain by-products which are undesirable for optical uses, for electrical uses, for heat stability uses where the presence of by-products or unreacted catalysts would cause degradation of the properties.

The silanes of this invention are useful as adhesion promoters or precursors which can be used to make other siloxane polymers by the use of mild hydrolysis. Such silanes can be of the following general formula (I):

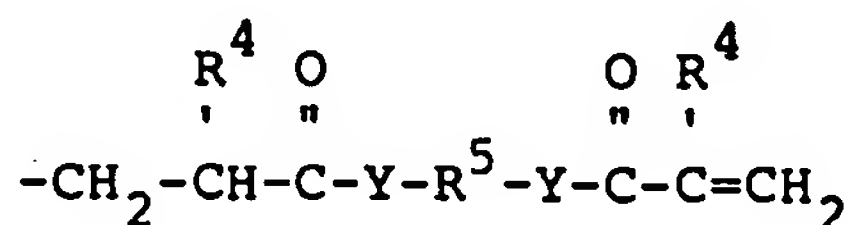


wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, and where the hydrogen of the =NH is substituted with an acryl functional group of the general formula

EP 0 230 342 B1



R¹ is hydrogen, an alkyl radical having from 1 to 4 carbon atoms per radical, or an acryl functional radical of the general formula



R² is a monovalent hydrocarbon radical or fluorinated alkyl radical,

X is a hydrolyzable group whose hydrolyzed groups do not form salts with the nitrogen atom,

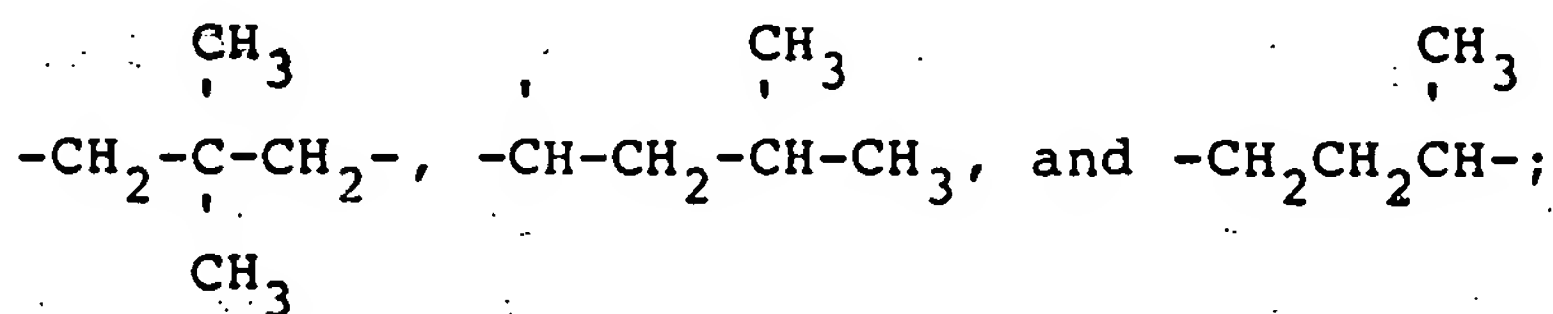
R⁴ is a hydrogen atom or a methyl radical,

R⁵ is a divalent hydrocarbon radical or divalent hydrocarbon radicals containing ether linkages,

Y is a divalent oxygen atom or -NR¹-,

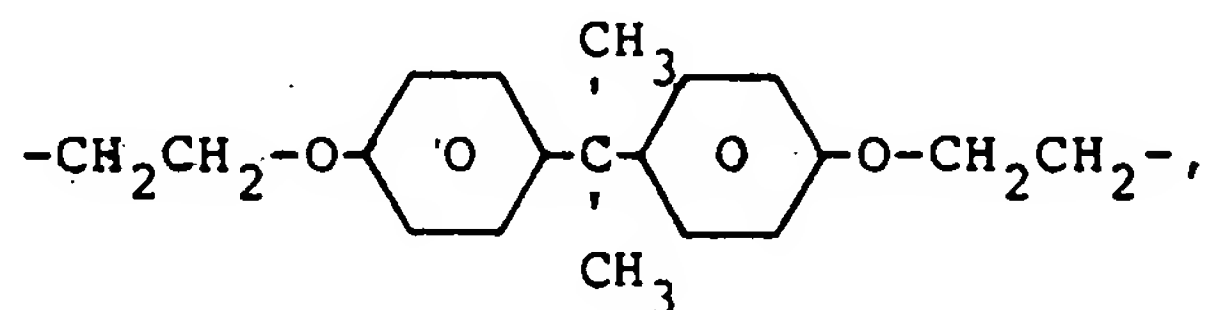
a is 1, 2, or 3.

R⁵ is a divalent hydrocarbon radical, for example, methylene, ethylene, propylene, butylene, hexylene, decylene,

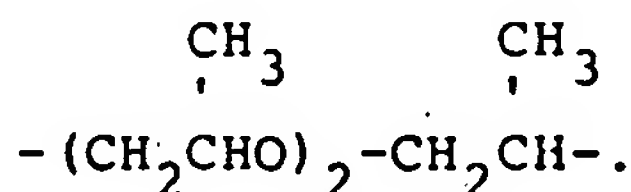


or a divalent hydrocarbon radical containing ether linkages, such as

-CH₂CH₂-O-CH₂CH₂-, -(CH₂CH₂O)₃-CH₂CH₂-, (CH₂CH₂CH₂O)₂-CH₂CH₂CH₂-, -(CH₂CH₂O)₈-CH₂CH₂-,



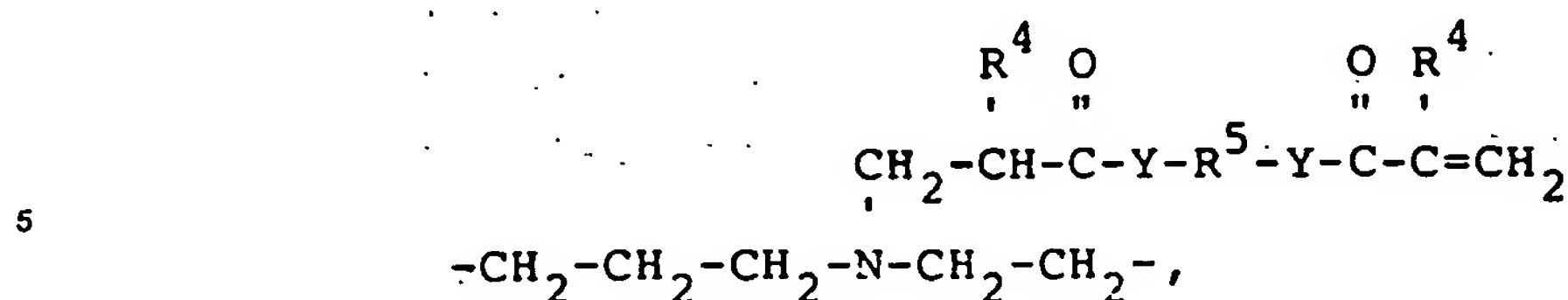
-(CH₂CH₂CH₂CH₂O)_{7,8}-CH₂CH₂CH₂CH₂-, -(CH₂CH₂O)₂-CH₂CH₂- and



Preferably, R is an alkylene radical of 3 to 10 carbon atoms or a radical of the formula -CH₂CH₂CH₂-NH-CH₂CH₂-, R² is methyl, X is OR³ in which R³ is an alkyl radical of from 1 to 8 carbon atoms or phenyl, R⁴ is hydrogen, R⁵ is a divalent hydrocarbon radical, Y is divalent oxygen atom, and a is 3.

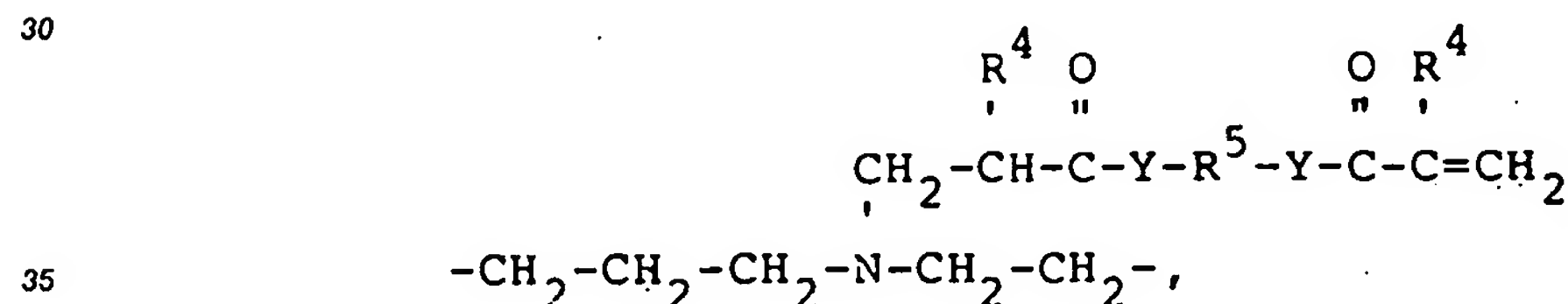
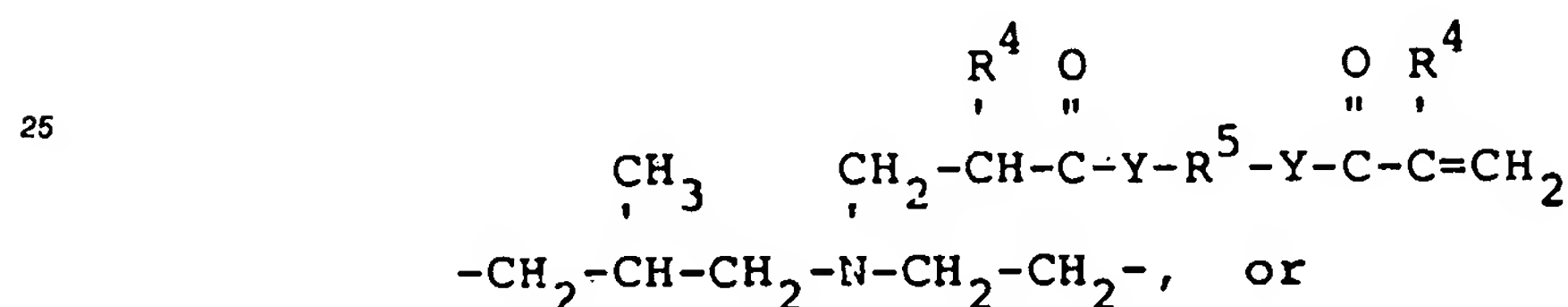
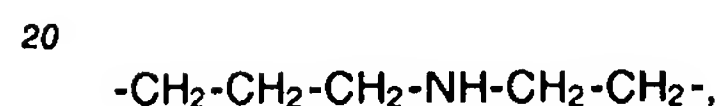
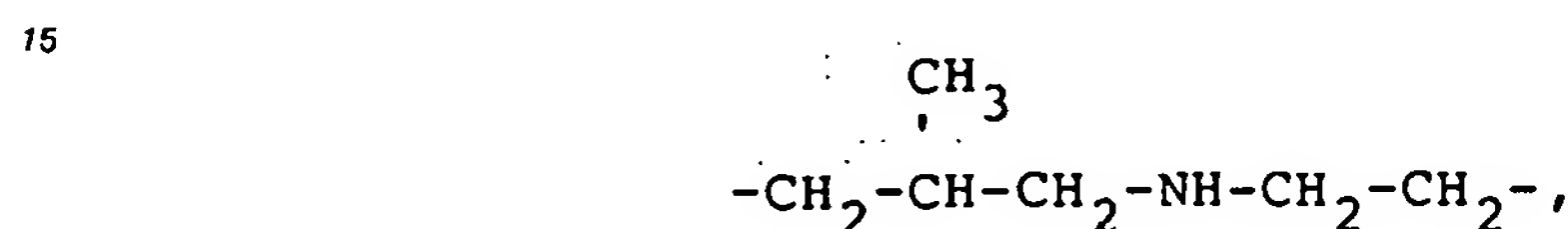
The siloxanes of the present invention have at least one acryl functional group per molecule. These siloxanes can be used to make coating compositions which cure when exposed to ultraviolet radiation. Such coating compositions can be hard and resin like or they can be elastomeric or gel-like. Each of these find useful applications in the art, such as in electronic coatings, in optical fiber coating, and as paper coatings. The concentration of the acryl groups on the siloxane, the molecular weight of the siloxane, and the other organic groups on the siloxane can determine the final characteristics of the acryl functional silicon

EP 0 230 342 B1



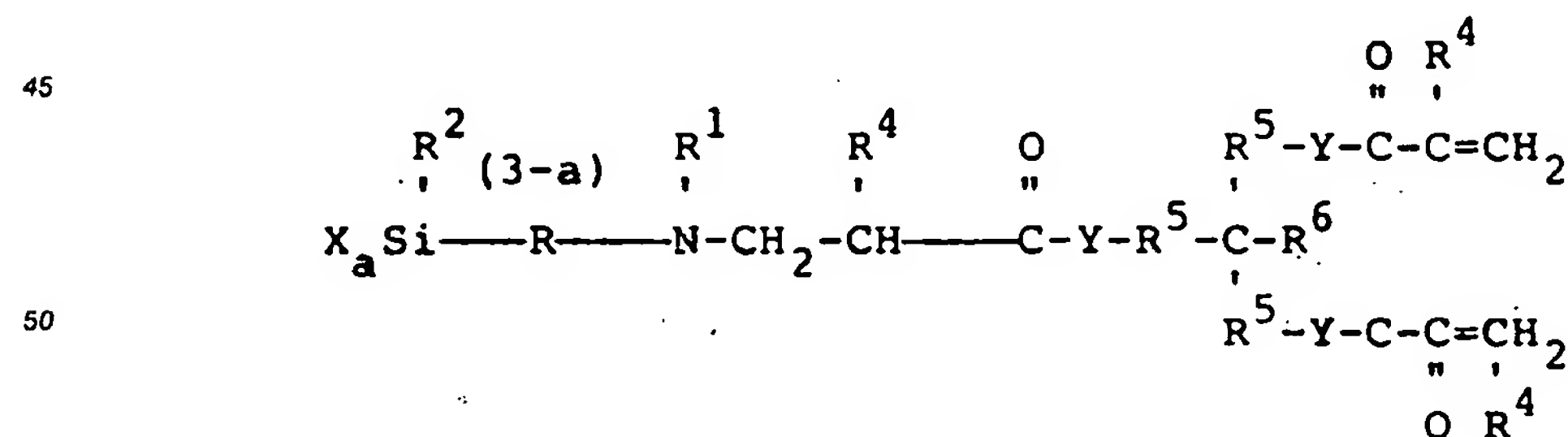
R¹ is methyl, R⁴ is hydrogen atom, Y is divalent oxygen atom, R⁵ is a divalent hydrocarbon radical of the general formula -(CH₂)_d- in which d is an integer of from 1 to 6 and there is an average of 10 to 300 dimethylsiloxane units per molecule.

Another type of siloxane containing acryl functionality is one in which there are from 2 to 20 acryl functional siloxane units per molecule in which a is 0, b is 1, R² is methyl, R is



R¹ is hydrogen atom, R⁴ is hydrogen atom, Y is divalent oxygen atom, R⁵ is a divalent hydrocarbon radical of the general formula -(CH₂)_d- in which d is an integer of from 1 to 6, there are two trimethylsiloxy units per molecule, and there is an average of from 100 to 500 dimethylsiloxane units per molecule.

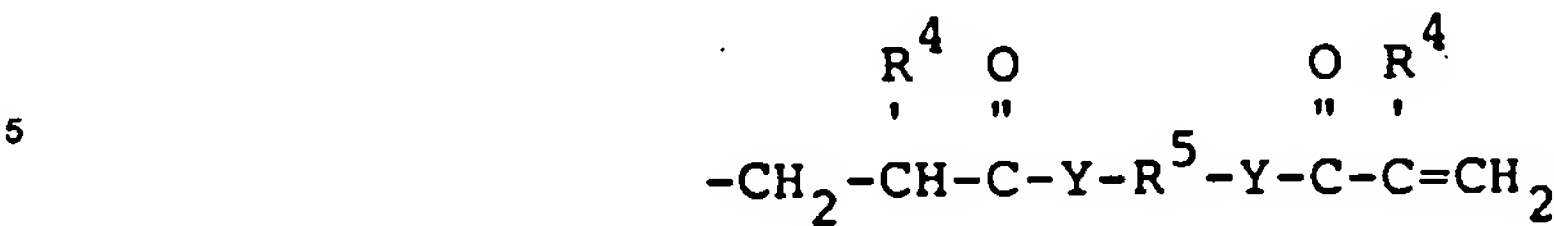
A type of preferred silane containing acryl functionality and made using tri- or tetra-acryl functional acryl compounds has the following general formula



wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms and where the hydrogen of the =NH is substituted with an acryl functional group of the

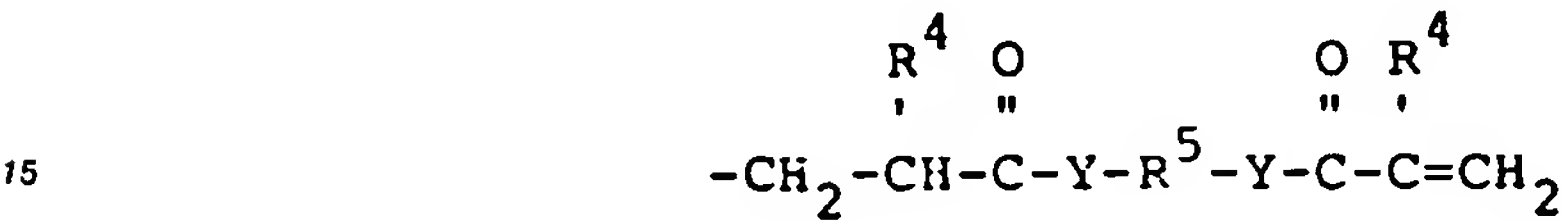
EP 0 230 342 B1

general formula



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R¹ is hydrogen, an alkyl radical having from 1 to 4 carbon atoms per radical, or an acryl functional radical of the general formula



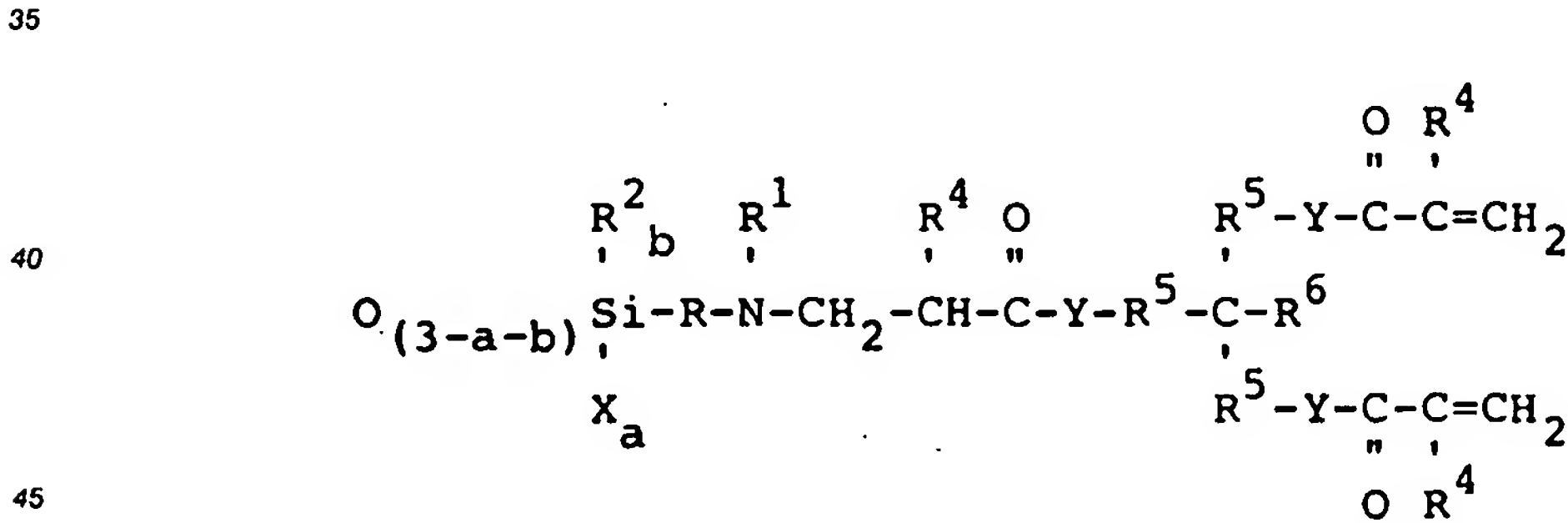
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R² is a monovalent hydrocarbon radical or fluorinated alkyl radical,
X is a hydrolyzable group whose hydrolyzed groups do not form salts with the nitrogen atom,
R⁴ is a hydrogen atom or a methyl radical,
R⁵ is a divalent hydrocarbon radical, divalent hydrocarbon radicals containing ether linkages,
R⁶ is a monovalent radical selected from the group consisting of a hydrocarbon radical, a hydroxyl substituted aliphatic hydrocarbon radical, and an acryl radical of the formula



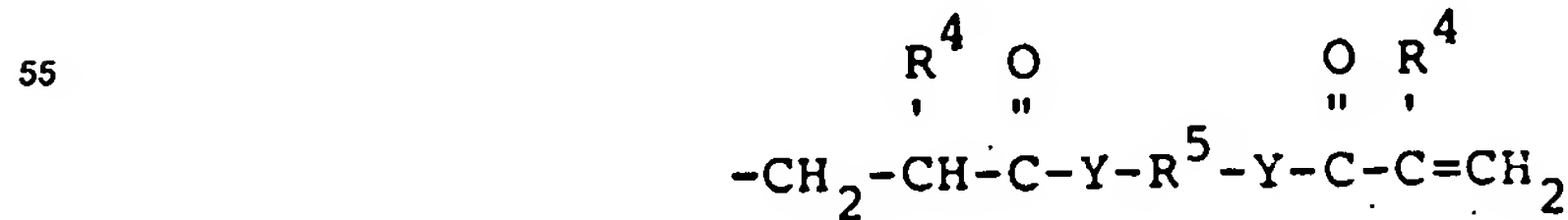
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Y is a divalent oxygen atom or -NR¹-,
a is 1, 2, or 3.
Siloxanes made from tri- or tetra-acryl functional compounds are those which have at least one siloxane unit of the following general unit formula



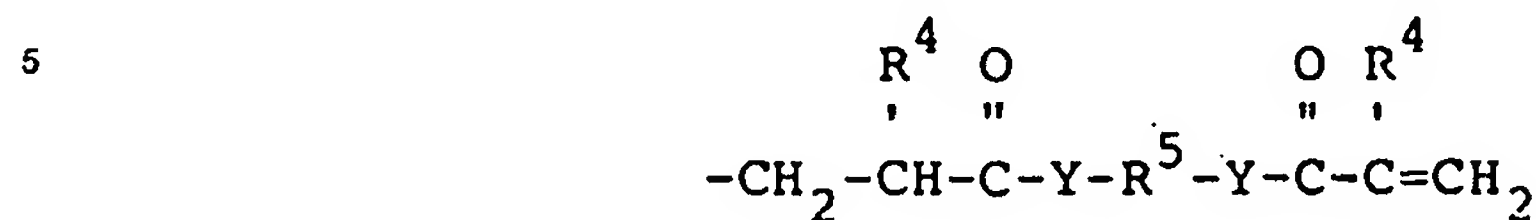
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wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, and where the hydrogen of the =NH is substituted with an acryl functional group of the general formula

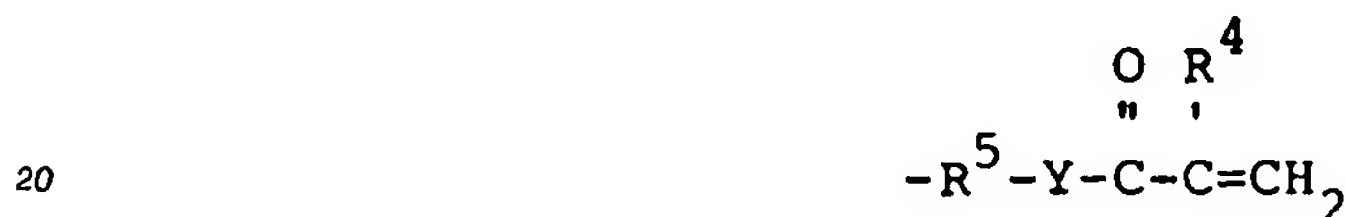


EP 0 230 342 B1

R¹ is hydrogen, an alkyl radical having from 1 to 4 carbon atoms per radical, or an acryl functional radical of the general formula



- R² is a monovalent hydrocarbon radical or fluorinated alkyl radical,
 X is a hydrolyzable group whose hydrolyzed groups do not form salts with the nitrogen atom,
 R⁴ is a hydrogen atom or a methyl radical,
 R⁵ is a divalent hydrocarbon radical, divalent hydrocarbon radicals containing ether linkages,
 R⁶ is a monovalent radical selected from the group consisting of a hydrocarbon radical, a hydroxyl
 substituted aliphatic hydrocarbon radical, and an acryl radical of the formula



- Y is a divalent oxygen atom or -NR¹-,
 a is 0, 1, or 2,
 \bar{b} is 0, 1, or 2, and
 $\bar{a} + \bar{b}$ is two or less, and any remaining siloxane units present in the polysiloxane are those having the general unit formula



in which R² is defined above and e is 0, 1, 2, or 3.

- The acryl functional siloxanes of this invention can be mixed with photoinitiator and then exposed to ultraviolet radiation to cause the siloxane to crosslink. The photo-initiator is used in amounts sufficient to provide the desired cure. Examples of photoinitiators include benzoin; benzoin alkyl ethers such as methyl, ethyl, isopropyl, and isobutyl benzoin ethers; acetophenone derivatives, such as dialkoxyacetophenone exemplified by diethoxyacetophenone, dichloroacetophenone, trichloroacetophenone, alpha,alpha-dimethoxyalpha-phenylacetophenone, 1-hydroxycyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenylpropane-1-one, methylphenyl glyoxylate, 4-benzoylbenzyl-trimethylammonium chloride, alpha-acyloxime esters such as 1-phenyl-1,2-propanedione-2-(O-ethoxycarbonyloxime), benzophenone in combination with a chain transfer agent such as a NH group and azo-bis(isobutyronitrile), benzil ketals, and ketone amine derivatives. Polysilanes are useful in the compositions which are to be cured by ultraviolet radiation. The polysilane photoinitiators are those which have a chain of catenated silicon atoms in either a linear configuration or in a ring configuration. The polysilane are soluble in the acryl functional siloxanes. The polysilanes can be the phenylmethylpolysilanes defined by West in U.S. Patent No. 4,260,780, issued April 7, 1981; the aminated methylpolysilanes defined by Baney et al. in U.S. Patent No. 4,314,956, issued February 9, 1982; the methylpolysilanes of Peterson et al. in U.S. Patent No. 4,276,424, issued June 30, 1981; and the polysilastyrene defined by West et al. in U.S. Patent No. 4,324,901, issued April 13, 1982.

- The compositions of acryl functional siloxane and photoinitiator can contain a storage stabilizer which can be amines, particularly tertiary amines such as diisopropylaminoethanol and trioctylamine. Another type of viscosity stabilizer is the free radical scavenger type, such as p-methoxyphenol (also known as hydroquinone, catechol, 4-t-butylcatechol, phenothiazine, hydroquinone, 2,6-di-t-butyl-p-methylphenol, and N-phenyl-2-naphthylamine. The free radical scavenger viscosity stabilizers are used in amounts of preferably zero to one weight percent based on the weight of the composition. If free radical scavenger is used the amounts should be small such as from 0.01 to 0.1 weight percent.

Compositions of this invention which are crosslinked or cured can contain optional ingredients which

EP 0 230 342 B1

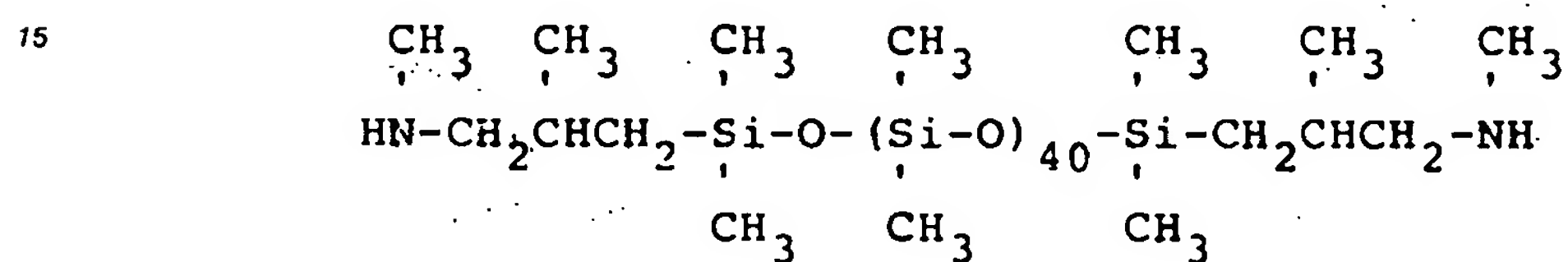
may be suitable for some applications. Examples of these optional ingredients include surfactants, reinforcing agents such as fillers and resins, colorants, heat stabilizers and other property modifiers.

As stated above, the compositions of this invention can be cured by other means which include exposure to electron beam radiation (does not require a photoinitiator), heating with peroxides and other methods which are known in the art to acryl functional compounds.

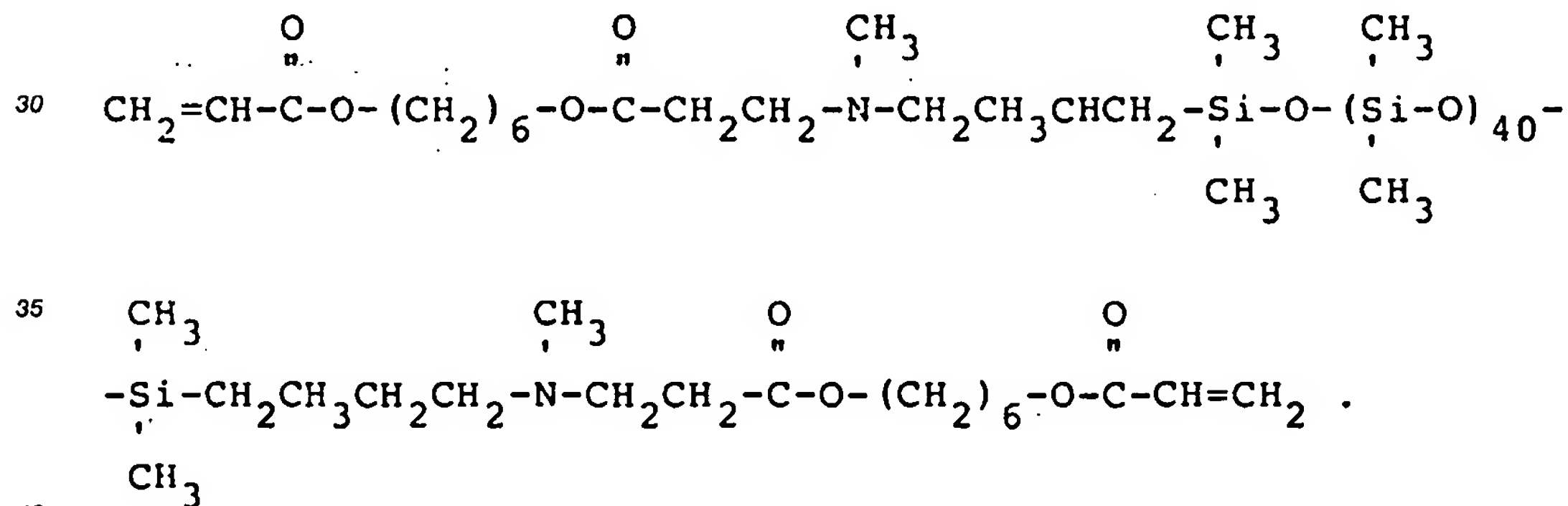
The following examples are present for illustrative purposes and should not be construed as limiting this invention which is properly delineated in the claims.

EXAMPLE 1

An acryl functional silicone was prepared by mixing 1,6-hexanediol diacrylate with an amine functional siloxane of the formula



in a ratio of one mole of amine per one mole of diacrylate molecule. The mixture was heated to 70 °C and this temperature was maintained for 23 hours at which time 80% of the diacrylate had disappeared. The mixture was initially cloudy but turned clear during the reaction. A photoinitiator, Darocure(TM) 1173 sold by E. M. Chemicals, in the amount of two weight percent was added to the reaction product. The reaction product is believed to have the formula



The Darocure 1173 has a formula

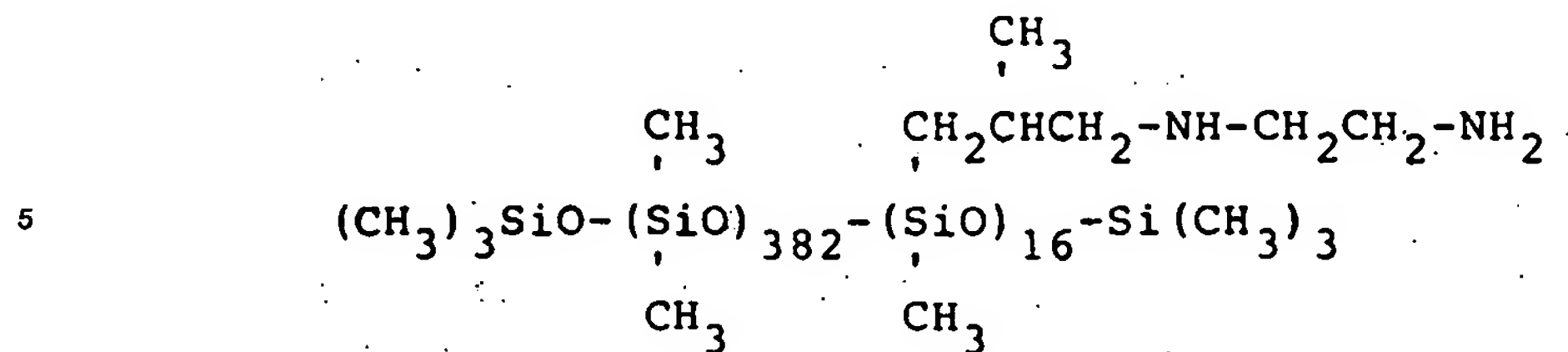


A film of the composition was cast and then exposed to ultraviolet radiation for 18 seconds. The resulting film had a tensile strength at break of 552 kilopascals with an elongation at break of 110%.

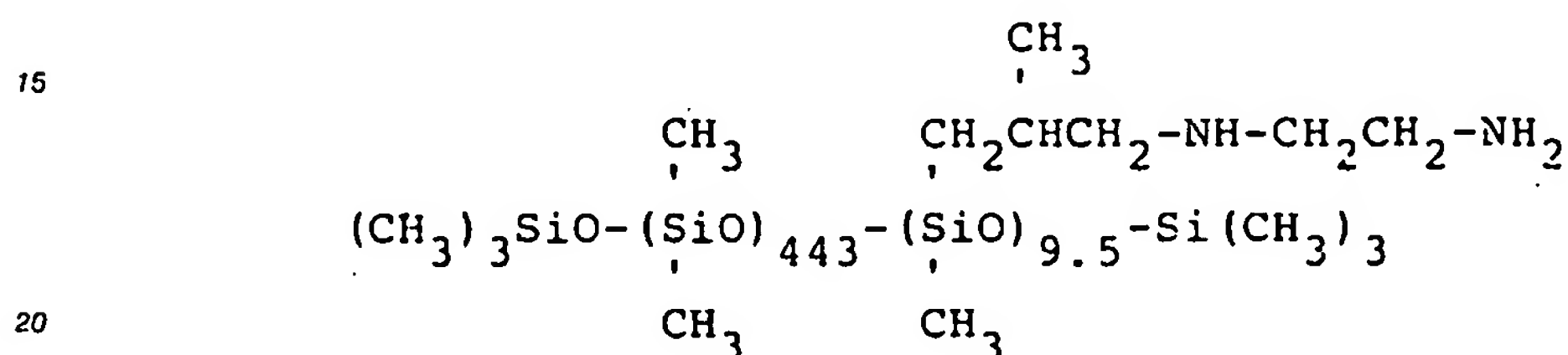
EXAMPLE 2

Acryl functional siloxane polymers were prepared by mixing the amounts shown in Table I into 10 g of an amine functional siloxane of the following average formula

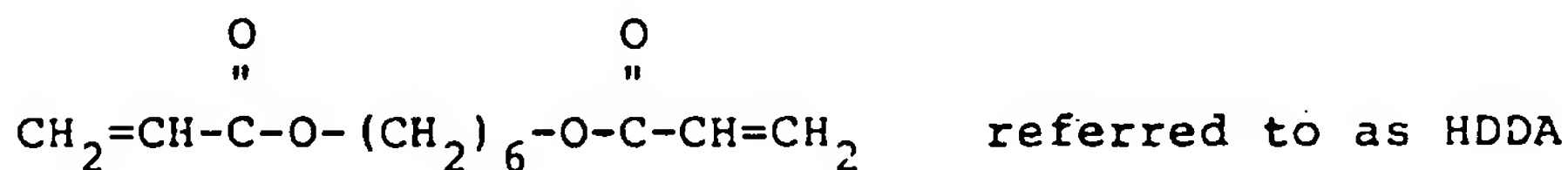
EP 0 230 342 B1



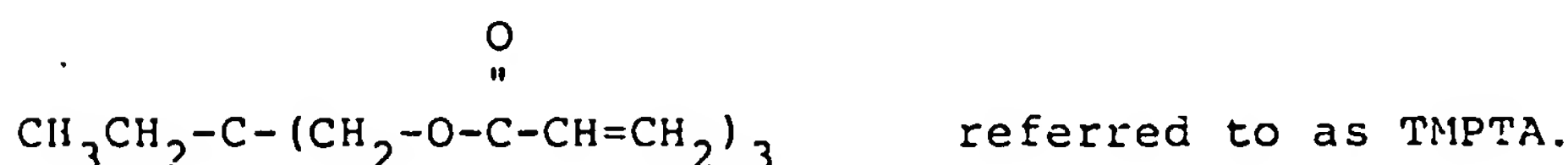
which is hereinafter referred to as Polymer A, or 10 g of an amine functional siloxane of the following average formula



which is hereinafter referred to as Polymer B, and one acryl functional compound from the following formulae



or



The mixtures were placed in capped vials and then heated in a convection oven at 70° C. The results were as shown in Table I. The mixtures were cloudy initially upon mixing the ingredients. These experiments show that the functionality of the amine containing silicon compound and the acryl functional compound need to be considered when making the acryl functional silicone compounds of this invention to ensure that the final products are those one wishes and can use. The shelf life of the reaction products in Table I were short but could be lengthened by adding either monofunctional acryl compound or an acid anhydride.

The reaction products of Run No. 5 and Run No. 7 were mixed with two weight percent of Darocure-(TM) 1173 and two weight percent of diisopropylaminoethanol, cast on aluminum Q-panels in a thickness of 8 mils, and then exposed to ultraviolet radiation. These compositions cured to elastomeric but weak films. The dry cured film using the reaction product of Run No. 5 had a cured film thickness of 5 mils and a tensile strength at break of 1165 kilopascals and an elongation at break of 21 %. The modulus at 2.5% was 145 kilopascals and at 5% was 296 kilopascals.

Run No. 5 was repeated except the ingredients were mixed and heated for 20 minutes at 70° C and then p-methoxyphenol in amounts of 150 ppm and 500 ppm and ethylhexyl acrylate in an amount of 1.73 g per 10 g of the reaction product were added to separate portions. In each case, the reaction product gelled within 24 hours. The free radical scavenger was not sufficient to achieve long shelf stability and the monofunctional acryl compound was neither enough or it was added to late during the reaction process. The following example will show that the monofunctional acryl compound can be used to increase the shelf stability of the reaction product. Also the presence of excess multi-functional acryl compound can be used to add shelf stability to the final reaction product.

EP 0 230 342 B1

EXAMPLE 3

An acryl functional silicone compound was prepared by mixing 25 g of Polymer A and 8.68 g of HDDA (1 mole HDDA per 1 mole amine hydrogen) and then heating at 70° C for 30 minutes at which time the mixture turned clear. The reaction product is hereinafter referred to as Product A.

A second acryl functional silicone compound was prepared by mixing 20 g of Polymer A and 13.88 g of HDDA (2 moles HDDA per 1 mole amine hydrogen) and then heating at 70° C for 30 minutes at which time the mixture was still cloudy. The reaction product is hereinafter referred to as Product B.

Products A and B were mixed with various amounts of ethylhexyl acrylate (EHA) and HDDA and then the shelf life was observed to determine the concentration of the acryl compounds which would exhibit increased shelf life before gelling occurred. The amounts of the acryl compounds added and the results of the shelf life observed are shown in Table II.

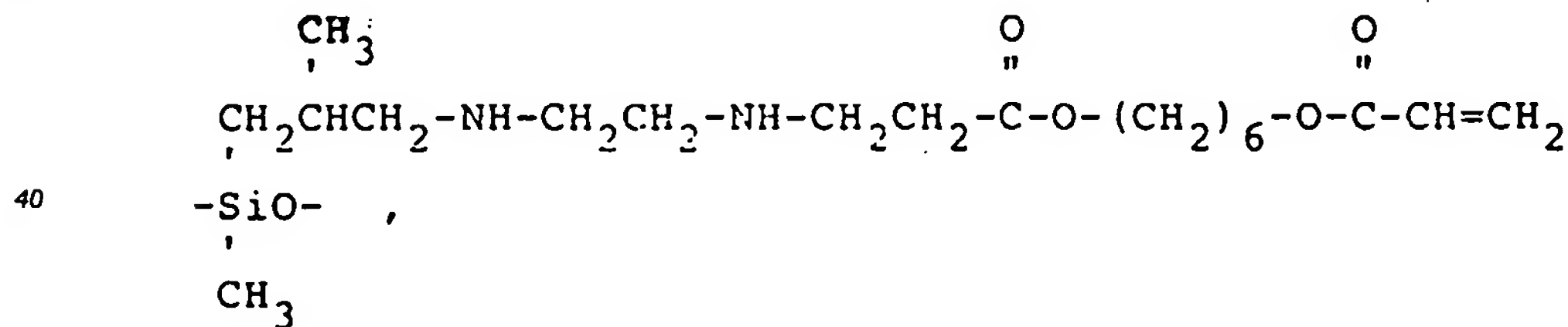
The tensile strength at break, the elongation at break, and the modulus were measured on compositions made by mixing the reaction products with two weight percent Darocure (TM) 1173 and two weight percent diisopropylaminoethanol, casting a film of about 8 mils thick on aluminum Q-panels, and then exposing the castings to ultraviolet radiation. The cured films had thicknesses of about 5 mils. The results were as shown in Table III.

EXAMPLE 4

Acryl functional siloxane polymers were prepared by mixing 10 g of Polymer A with 5.21 g of HDDA. This mixture was opaque initially. Without any additives, this mixture formed a reaction product which was a cloudy gel in about 2.5 hours at room temperature. Ethanol was added to another sample of this mixture in the amount of 1.52 g, and this mixture formed a clear reaction product which gelled in about 40 minutes at room temperature. Another mixture was prepared by mixing Polymer A and HDDA as described above with 1.52 g of toluene, which formed a clear reaction product at room temperature which gelled between 2.5 and 24 hours. A fourth mixture was prepared by combining Polymer A and HDDA with 1.52 g of isopropyl alcohol. This mixture formed a clear reaction product which gelled in about 2.5 hours. In every case, heating the reaction resulted in a clear gel. The addition of ethanol and isopropyl alcohol increased the rate of the reaction as indicated by the rapid formation of a clear reaction product.

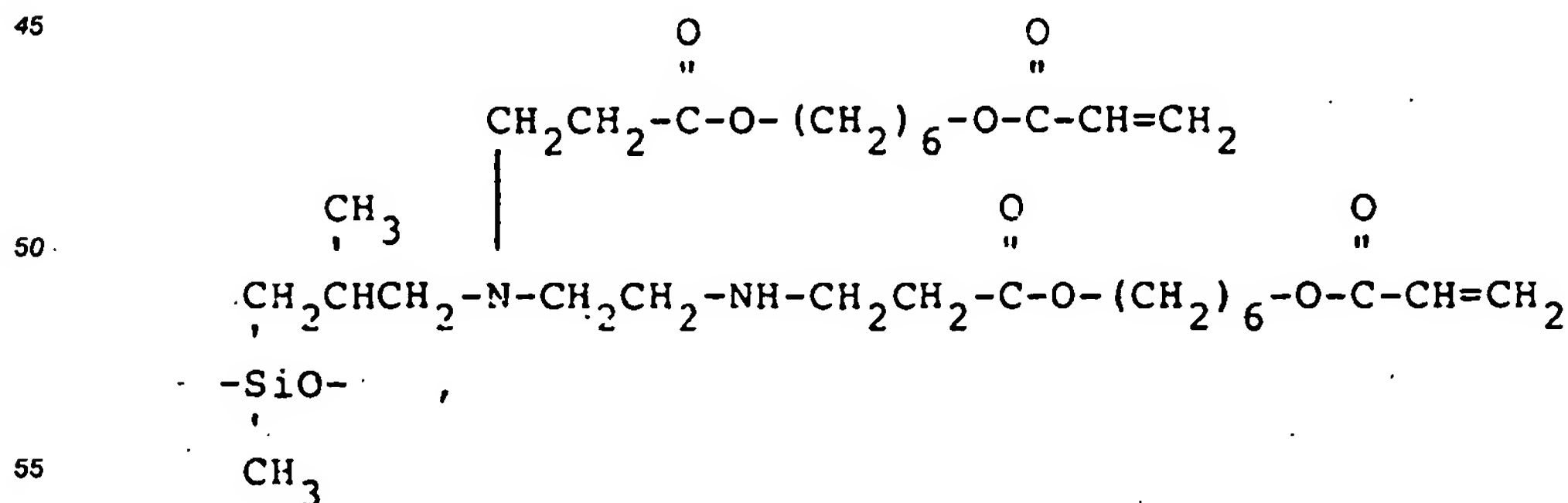
The reaction product is believed to be a siloxane polymer of the structure of Polymer A in which the amine hydrogens are reacted with HDDA and in which the following siloxane units are present, namely trimethylsiloxy units, dimethylsiloxane units,

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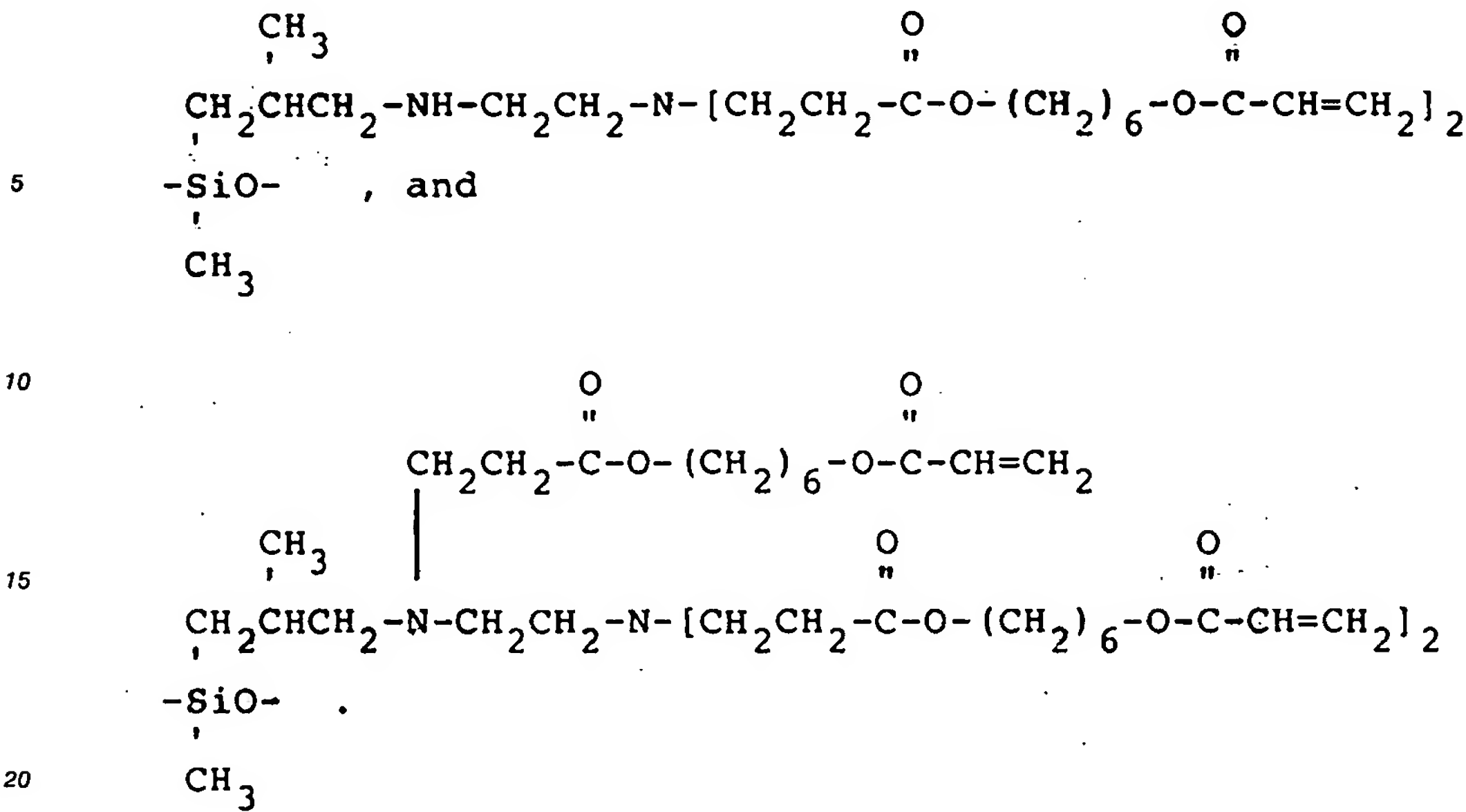
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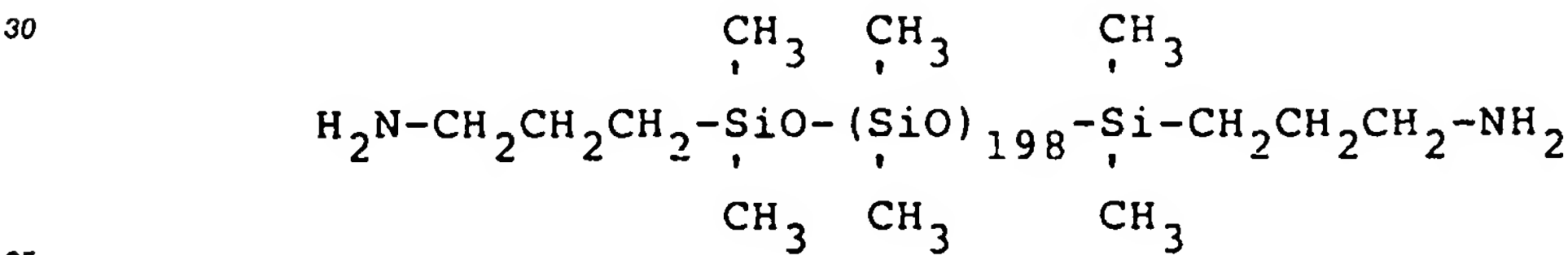
EP 0 230 342 B1



These siloxane units are randomly distributed along the polymer chain.

25 EXAMPLE 5

Two acryl functional siloxane polymers were prepared by mixing 7 g of an amine functional polymer of the following formula



which is hereinafter referred to as Polymer C, 0.63 g of HDDA, 0.37 g of ethanol, and 0.019 cc of a 1 % solution of p-methoxyphenol. One of these mixtures was mixed and maintained at room temperature and after 60 minutes the mixture was still cloudy but more viscous. This reaction product is referred to as Product C. The other mixture was mixed and was initially cloudy but after heating at 60° C for 15 minutes the mixture became clear and remained clear after 60 minutes of heating but became cloudy upon cooling to room temperature. This reaction product is referred to as Product D. A third mixture was prepared as described above in this example except that 0.74 g of ethanol was used instead of the 0.37 g. This mixture was mixed and maintained at room temperature. It was somewhat cloudy initially but became clear after 60 minutes. This reaction product is referred to as Product E. To each of the reaction products, 3.0 g of isobornyl acrylate and 0.2 g of Darocure(TM) 1173 was added. Each of the reaction products became clear fluids which had a viscosity at 25° C in the range of 0.5 to 1.0 Pa.s and a shelf life of >4 days. Films of these compositions were deposited and then exposed to ultraviolet radiation while under a blanket of nitrogen gas. The cured films had the properties shown in Table IV and were elastomeric.

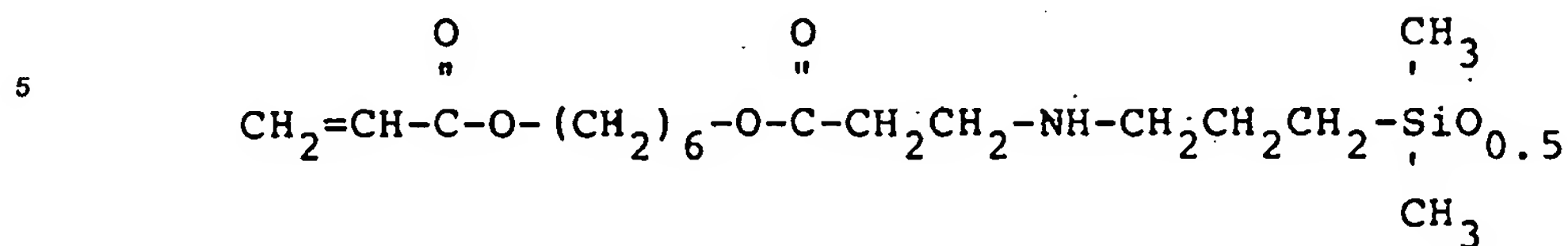
TABLE IV

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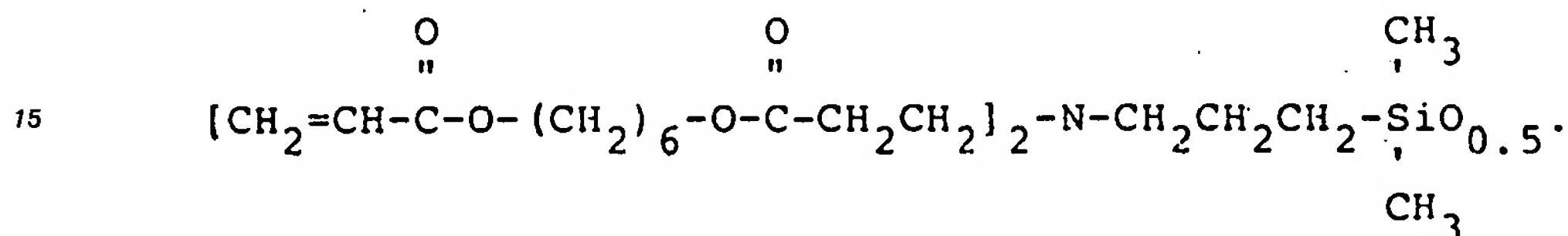
PRODUCT	TENSILE STRENGTH,kPa	ELONGATION, %	MODULUS kPa, AT 2.5%
C	1965	102	593
D	2772	133	669
E	2717	120	717

EP 0 230 342 B1

The reaction products are believed to have the following endblocking siloxane units



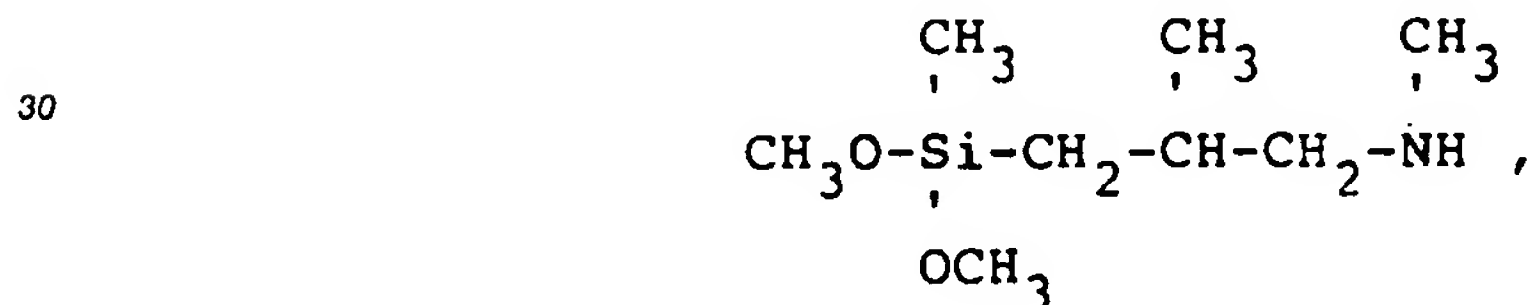
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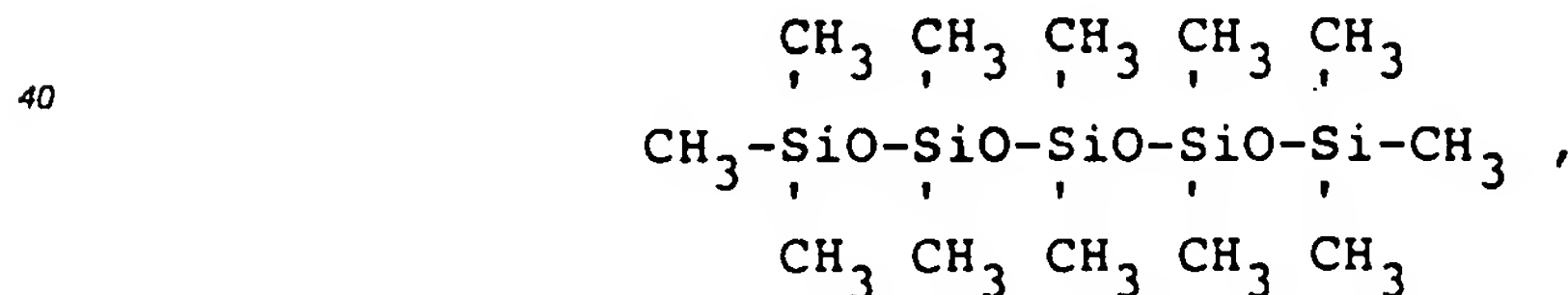
It is also believed that there would be endblocking units in which the isobornyl acrylate reacted with the amine hydrogen atoms which had not yet reacted with HDDA at the time the isobornyl acrylate was added.

EXAMPLE 6

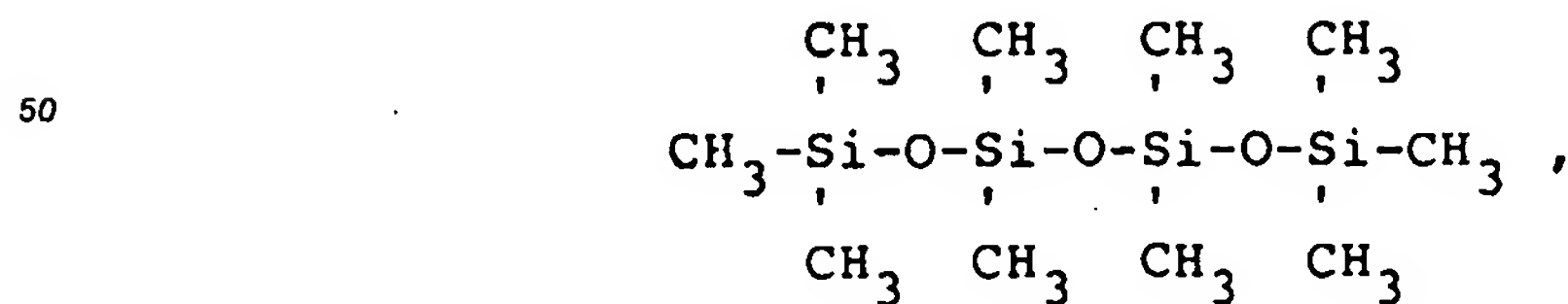
Acryl functional silane was prepared by mixing at room temperature 0.64 g of an amine silane of the formula



0.37 g of HDDA, 3.0 g of siloxane as solvent of the formula



0.5 g of the following siloxane as an internal standard for the gas chromatogram



and 0.5 g of the solvents shown in Table V to show whether the solvent has an effect on the reaction rate, i.e. a promoter solvent. Also shown in Table V is the percentage disappearance of the amine and the HDDA which was an indication of the completion of the reaction.

EP 0 230 342 B1

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TABLE I				COMMENTS
RUN NO., POLYMER	TMPTA, GRAMS	HDDA, GRAMS	MOLES ACRYL COMPOUND MOLES AMINE HYDROGEN	
1,A	4.55	----	1/1	Medium gel formed in 10 minutes
2,A	1.52	----	1/3	Hard gel formed in 10 minutes
3,A	----	3.47	1/1	Clear in 30 minutes soft gel in 60 minutes
4,A	----	1.74	1/3	Clear in 10 minutes gel in 30 to 60 min
5,A	----	3.47	1/1	Clear in 45 minutes soft gel in 60 min
6,A	----	5.21	1.5/1	Cloudy, viscous after 60 minutes gelled on cooling
7,B	----	2.48	1.5/1	Opaque after 60 minutes gelled in 2 days

EP 0 230 342 B1

TABLE II

	RUN NO., PRODUCT	GRAMS PRODUCT	EHA, GRAMS	OBSERVATION
5	8,A	10	0.0	Clear, gelled in <1 hour
	9,A	9	1.0	Clear, gelled in ca. 1 hour
	10,A	7	3.0	Clear, gelled in ca. 20 hours
	11,B	10	0.0	Cloudy, gelled in ca. 2.25 hours
	12,B	9	1.0	Clear, gelled in ca. 20 hours
10	13,B	7	3.0	Clear, fluid after 20 hours, gelled in ca. 2 days

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EP 0 230 342 B1

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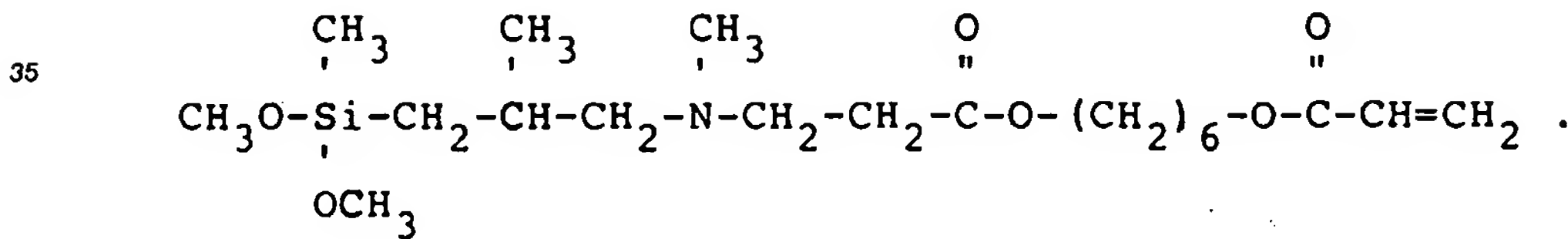
TABLE III				
COMPOSITION	PRODUCT FROM RUN NO.	TENSILE, kPa	ELONGATION, %	MODULUS, AT 2.5%
14	11	2020	13	427
15	12	2848	18	469
16	13	1634	19	234
				862
				938
				462

EP 0 230 342 B1

TABLE V

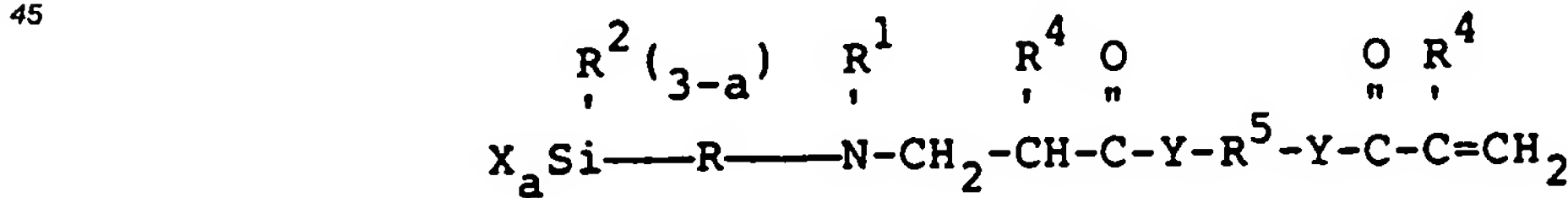
	SOLVENT	REACTION TIME	PERCENT DISAPPEARANCE AMINE	HDDA
5	ISOPROPYL ALCOHOL	0 min	0.0	0.0
		32 min	6.6	8.8
		68 min	16.6	23.0
10		114 min	26.4	35.8
		71 hours	99.3	100.0
15	$\begin{array}{ccccc} \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\ & & & & \\ \text{CH}_3-\text{Si}-\text{O}-(\text{Si}-\text{O})_3-\text{Si}-\text{CH}_3 \\ & & & & \\ \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \end{array}$	0 min	0.0	0.0
		35 min	3.1	3.1
		109 min	8.0	7.1
20		19 hours	27.6	44.9
		67 hours	46.0	75.7
25	TOLUENE	0 min	0.0	0.0
		67.5 hours	41.6	69.8
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The reaction product of these reactions is believed to be silanes of the following formula



40 The reaction of the amine silane and the HDDA shows that the alcohol greatly increases the rate of the reaction.

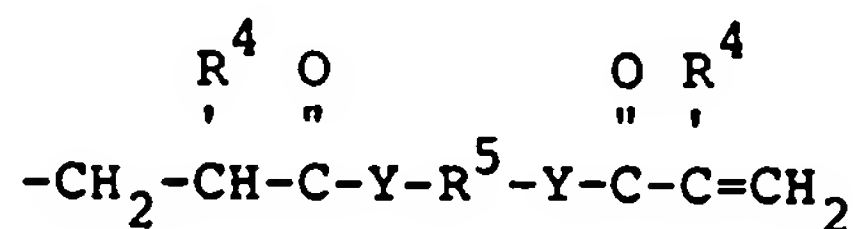
1. An acryl functional silicone compound in which the compound is a silane having the following formula



50 wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, and where the hydrogen of the =NH is substituted with an acryl functional group of the general formula

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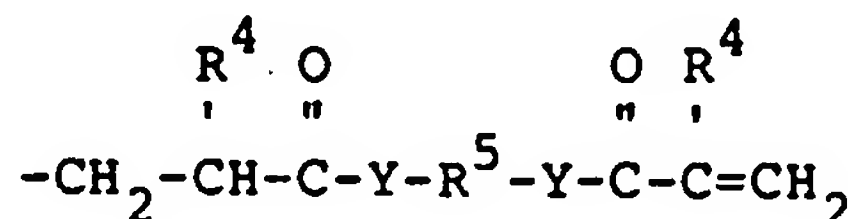
EP 0 230 342 B1



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R¹ is hydrogen, an alkyl radical having from 1 to 4 carbon atoms per radical, or an acryl functional radical of the general formula

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R² is a monovalent hydrocarbon radical or fluorinated alkyl radical,

X is a hydrolyzable group whose hydrolyzed groups do not form salts containing a nitrogen atom,

R⁴ is a hydrogen atom or a methyl radical,

R⁵ is a divalent hydrocarbon radical or divalent hydrocarbon radicals containing ether linkages,

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Y is a divalent oxygen atom or -NR¹-,

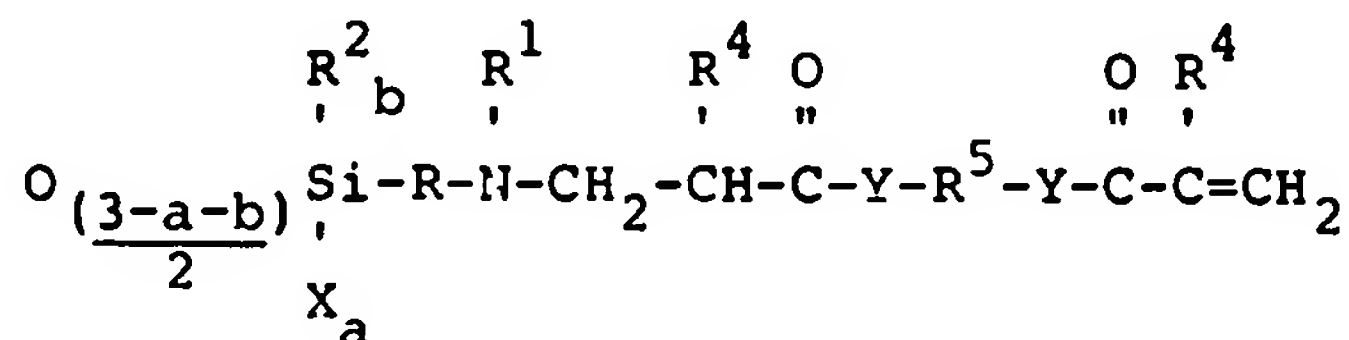
a is 1, 2, or 3.

2. The acryl functional silicone compound according to claim 1 in which R is an alkylene radical having from 3 to 10 carbon atoms per radical, R² is methyl, X is OR³ in which R³ is an alkyl radical of from 1 to 8 carbon radicals per radical or phenyl, R⁴ is a hydrogen atom, R⁵ is a divalent hydrocarbon radical, Y is a divalent oxygen atom, and a is 3.

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3. An acryl functional silicone compound in which the compound is a polysiloxane having at least one acryl functional siloxane unit of the general unit formula

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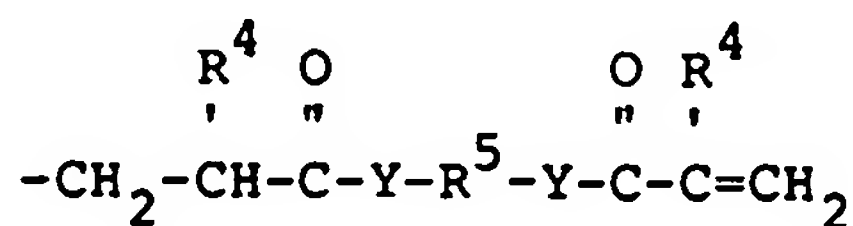


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wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula =NH in which the two bonds of the =NH are bonded to carbon atoms, and where the hydrogen of the =NH is substituted with an acryl functional group of the general formula

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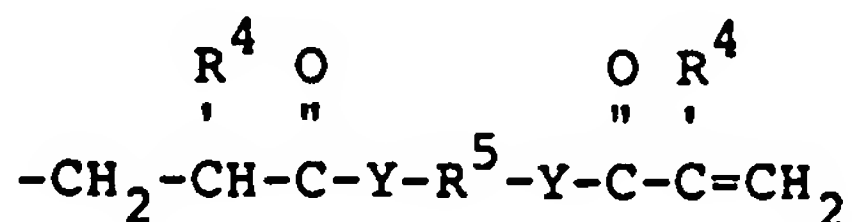
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R¹ is an alkyl radical having from 1 to 4 carbon atoms per radical, an acryl functional radical of the general formula

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EP 0 230 342 B1

R² is a monovalent hydrocarbon radical or fluorinated alkyl radical,

X is a hydrolyzable group whose hydrolyzed groups do not form salts containing a nitrogen atom,

R⁴ is a hydrogen atom or a methyl radical,

R⁵ is a divalent hydrocarbon radical or divalent hydrocarbon radicals containing ether linkages,

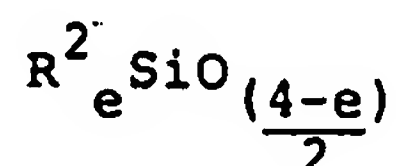
5 Y is a divalent oxygen atom or -NR¹-,

a is 0, 1, or 2,

b is 0, 1, or 2, and

a + b is two or less, and any remaining siloxane units present in the polysiloxane are those having the general unit formula

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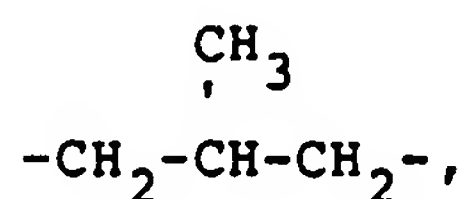


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in which R² is defined above and e is 0, 1, 2, or 3.

4. The polysiloxane according to claim 3 in which there are two acryl functional siloxane units per molecule in which a is 0, b is 2, R² is methyl, R is

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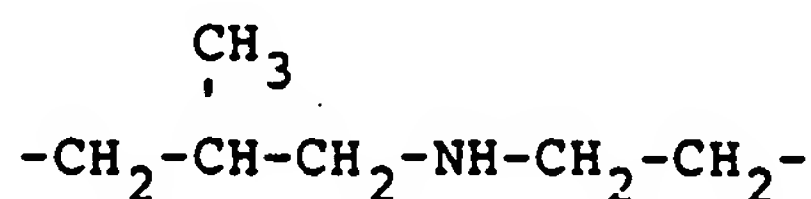
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R¹ is methyl, R⁴ is hydrogen atom, Y is divalent oxygen atom, R⁵ is a divalent hydrocarbon radical of the general formula -(CH₂)_d- in which d is an integer of from 1 to 6 and there is an average of 10 to 300 dimethylsiloxane units per molecule.

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5. The polysiloxane according to claim 3 in which there are from 2 to 20 acryl functional siloxane units per molecule in which a is 0, b is 1, R² is methyl, R is

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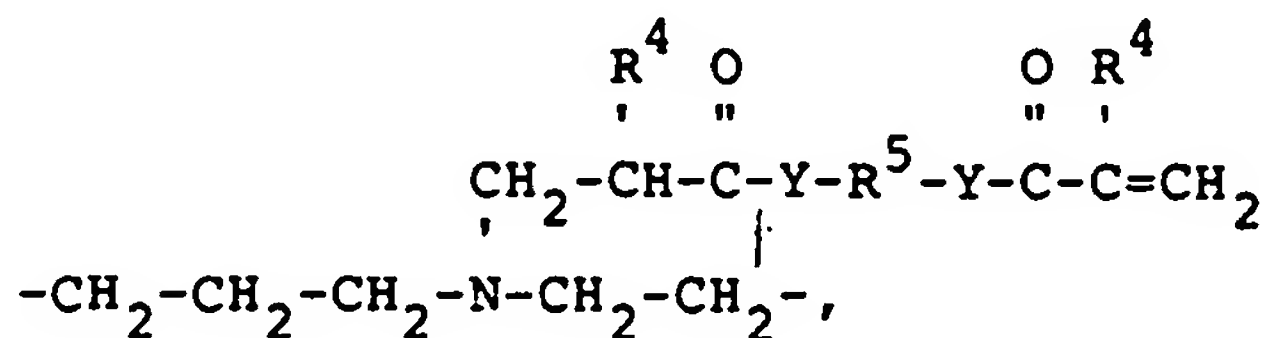


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R⁴ is hydrogen atom, Y is divalent oxygen atom, R⁵ is a divalent hydrocarbon radical of the general formula -(CH₂)_d- in which d is an integer of from 1 to 6, there are two trimethylsiloxy units per molecule, and there is an average of from 100 to 500 dimethylsiloxane units per molecule.

6. The polysiloxane according to claim 3 in which there are two acryl functional siloxane units per molecule in which a is 0, b is 2, R² is methyl, R is

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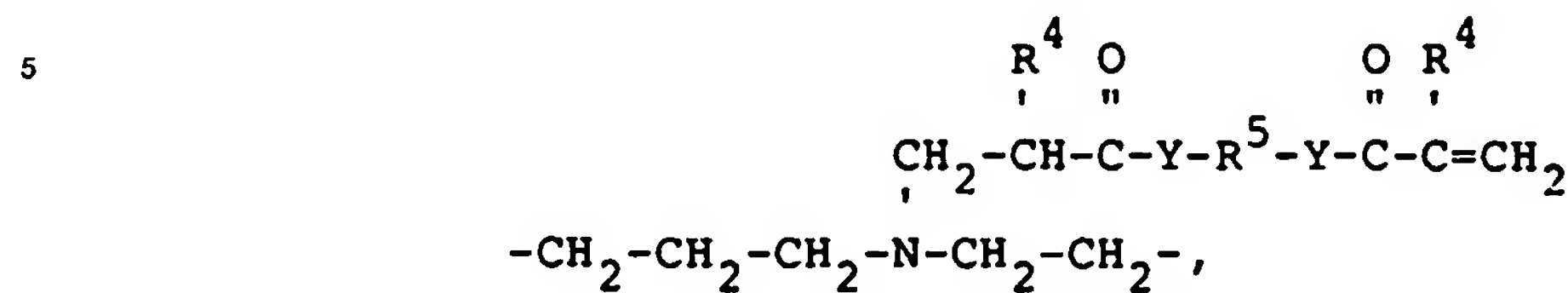
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R¹ is methyl, R⁴ is hydrogen atom, Y is divalent oxygen atom, R⁵ is a divalent hydrocarbon radical of the general formula -(CH₂)_d- in which d is an integer of from 1 to 6 and there is an average of 10 to 300 dimethylsiloxane units per molecule.

EP 0 230 342 B1

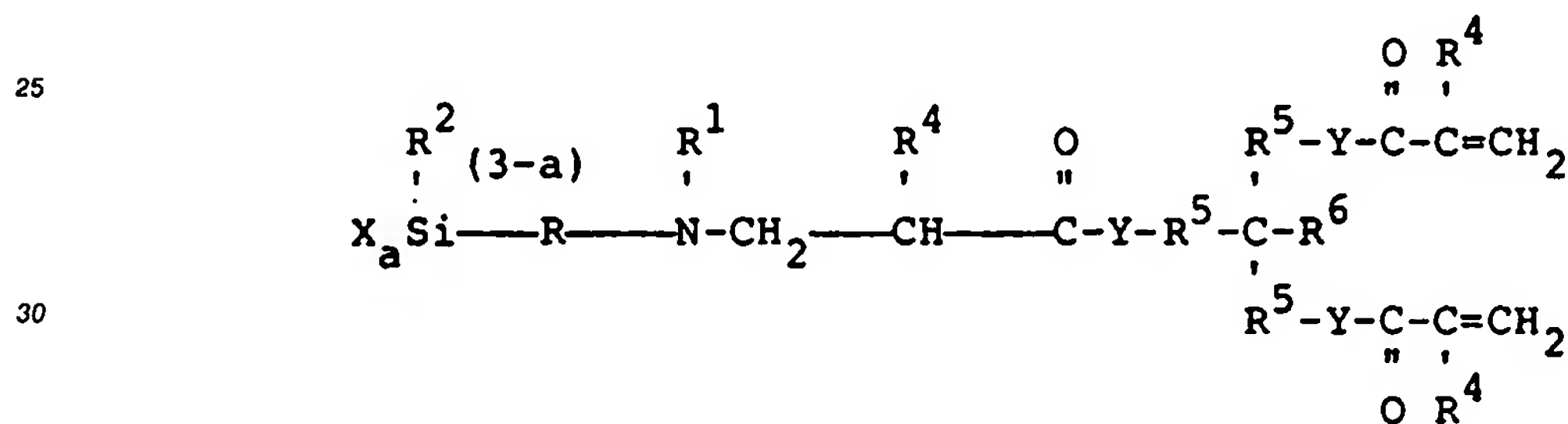
7. The polysiloxane according to claim 3 in which there are from 2 to 20 acryl functional siloxane units per molecule in which \underline{a} is 0, \underline{b} is 1, R^2 is methyl, R is



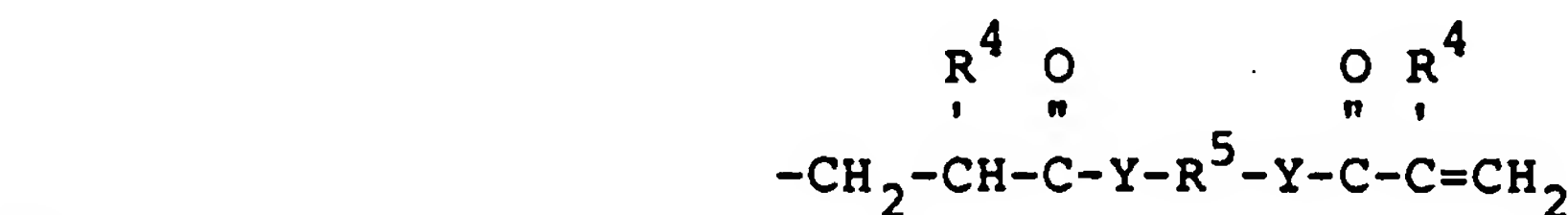
R^4 is hydrogen atom, Y is divalent oxygen atom, R^5 is a divalent hydrocarbon radical of the general formula $-(\text{CH}_2)_d-$ in which d is an integer of from 1 to 6, there are two trimethylsiloxy units per molecule, and there is an average of from 100 to 500 dimethylsiloxane units per molecule.

8. The polysiloxane according to claim 3 in which there are two acryl functional siloxane units per molecule in which a is 0, b is 2, R^2 is methyl, R is $-\text{CH}_2 - \text{CH}_2 - \text{CH}_2 -$, R^1 is methyl, R^4 is hydrogen atom, Y is divalent oxygen atom, R^5 is a divalent hydrocarbon radical of the general formula $-(\text{CH}_2)_d-$ in which d is an integer of from 1 to 6 and there is an average of 10 to 300 dimethylsiloxane units per molecule.

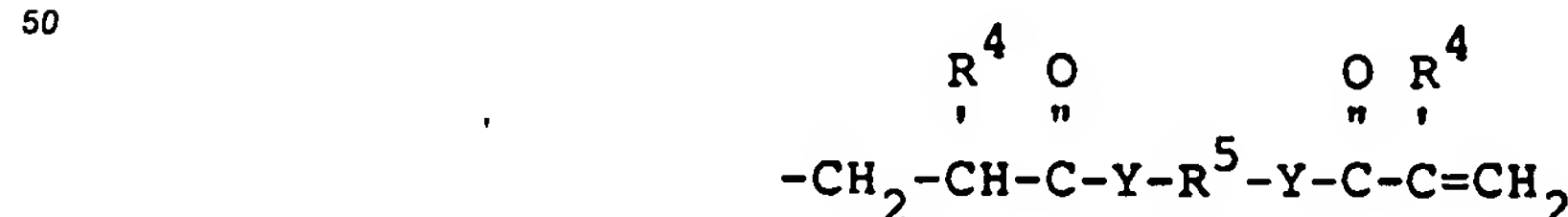
9. An acryl functional silicone compound in which the compound is a silane having the following general formula



wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula $=\text{NH}$ in which the two bonds of the $=\text{NH}$ are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula $=\text{NH}$ in which the two bonds of the $=\text{NH}$ are bonded to carbon atoms, and where the hydrogen of the $=\text{NH}$ is substituted with an acryl functional group of the general formula



R^1 is hydrogen, an alkyl radical having from 1 to 4 carbon atoms per radical, or an acryl functional radical of the general formula

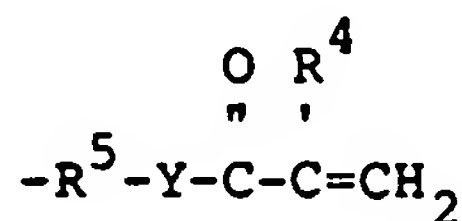


R^2 is a monovalent hydrocarbon radical or fluorinated alkyl radical,
X is a hydrolyzable group whose hydrolyzed groups do not form salts containing a nitrogen atom,
 R^4 is a hydrogen atom or a methyl radical,

EP 0 230 342 B1

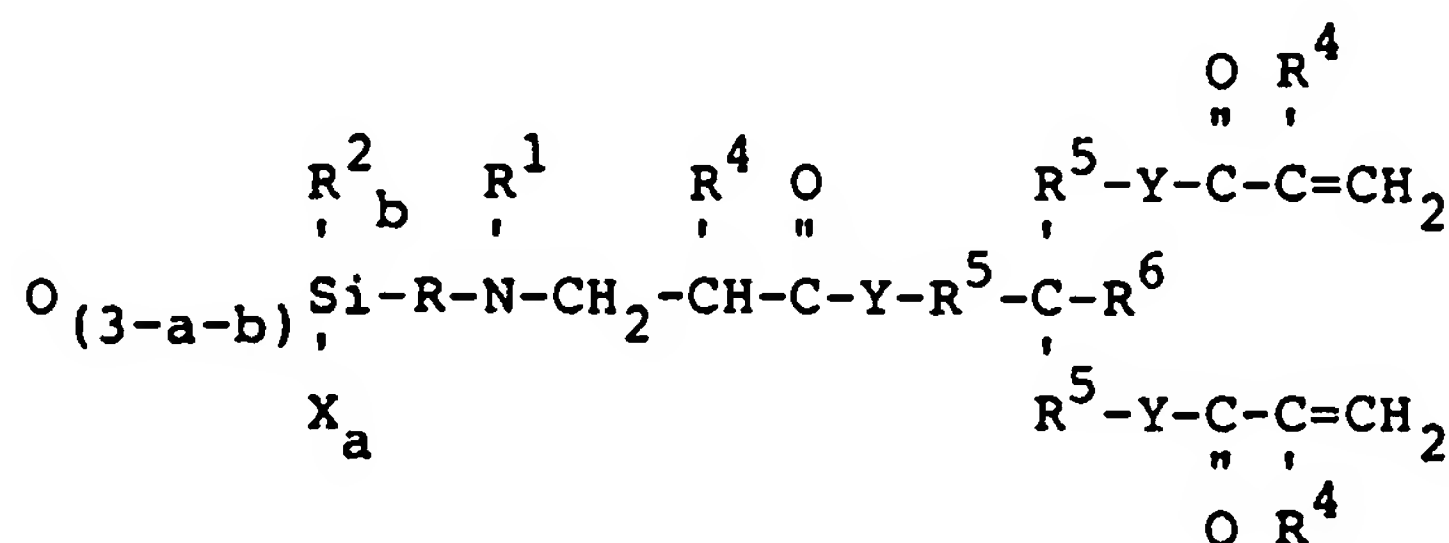
R^5 is a divalent hydrocarbon radical or divalent hydrocarbon radicals containing ether linkages,

R^6 is a monovalent radical selected from the group consisting of a hydrocarbon radical, a hydroxyl substituted aliphatic hydrocarbon radical, and an acryl radical of the formula

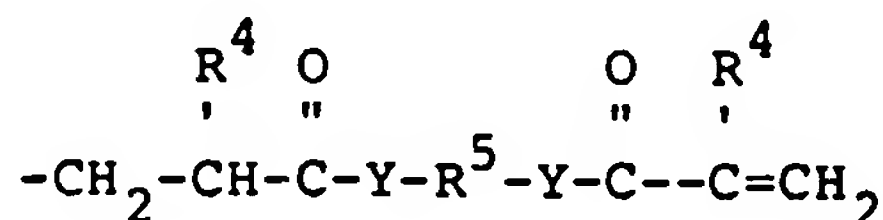


Y is a divalent oxygen atom or $-\text{NR}^1-$,
a is 1, 2, or 3.

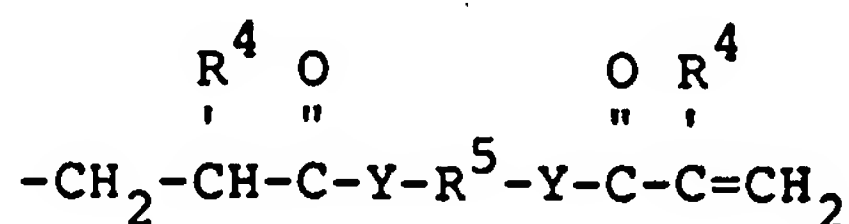
10. An acryl functional silicone compound in which the compound is a siloxane having at least one unit of the following general unit formula



wherein R is a divalent hydrocarbon radical, a divalent hydrocarbon radical having amino functionality of the formula $=\text{NH}$ in which the two bonds of the $=\text{NH}$ are bonded to carbon atoms, or a divalent hydrocarbon radical having amino functionality of the formula $=\text{NH}$ in which the two bonds of the $=\text{NH}$ are bonded to carbon atoms, and where the hydrogen of the $=\text{NH}$ is substituted with an acryl functional group of the general formula



R^1 is an alkyl radical having from 1 to 4 carbon atoms per radical, or an acryl functional radical of the general formula



R^2 is a monovalent hydrocarbon radical or fluorinated alkyl radical,

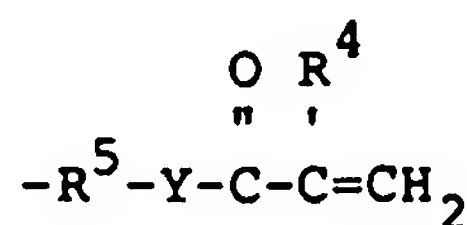
X is a hydrolyzable group whose hydrolyzed groups do not form salts containing a nitrogen atom,

R^4 is a hydrogen atom or a methyl radical,

R^5 is a divalent hydrocarbon radical or divalent hydrocarbon radicals containing ether linkages,

R^6 is a monovalent radical selected from the group consisting of a hydrocarbon radical, a hydroxyl substituted aliphatic hydrocarbon radical, and an acryl radical of the formula

EP 0 230 342 B1



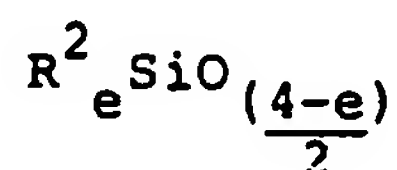
5

Y is a divalent oxygen atom or -NR¹-,

a is 0, 1, or 2,

b is 0, 1, or 2, and

10 $\bar{a} + b$ is two or less, and any remaining siloxane units present in the polysiloxane are those having the general unit formula

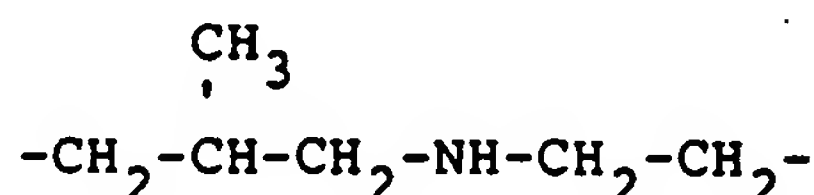


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in which R² is defined above and e is 0, 1, 2, or 3.

20 11. The polysiloxane according to claim 10 in which there are from 2 to 20 acryl functional siloxane units in which a is 0, b is 1, R is

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30 R⁴ is hydrogen atom, Y is divalent oxygen atom, R⁵ is a divalent hydrocarbon radical of the general formula -(CH₂)_d- in which d is an integer of from 1 to 6, and R⁶ is ethyl, there are two trimethylsiloxy units per molecule, and there is an average of from 100 to 500 dimethylsiloxane units per molecule.

35 12. A method of preparing an acryl functional silicone compound as claimed in claim 1 or 3, comprising forming an intimate mixture of an amino functional silicon compound in which the amino group is a primary amine or a secondary amine and an acryl functional compound having at least two acrylate, methacrylate, acrylamide, or methacrylamide groups per molecule at a temperature less than 100°C for a time sufficient to produce an acryl functional silicone compound in which at least one silicon atom having an acryl functional radical bonded to the silicon atom through a silicon-carbon bond, where the acryl functional radical contains at least one carbon-nitrogen-carbon bond and an acrylate, methacrylate, 40 acrylamide, or methacrylamide groups any other groups bonded to the silicon atom being monovalent hydrocarbon radicals, fluorinated alkyl radicals, hydrolyzable groups whose hydrolyzed groups do not form a salt containing a nitrogen atom, divalent oxygen atoms which bond two silicon atoms in an Si-O-Si linkage, divalent hydrocarbon radicals, bonding at least two silicon atoms together, and silicon atoms which are present and which do not have an acryl functional radical bonded thereto can have any of the 45 other groups bonded to them as stated herein.

13. The method according to claim 12 in which the intimate mixture is heated to a temperature above 25°C but not exceeding 100°C.

50 14. The method according to claim 12 or 13, further comprising a promotor solvent in the mixture.

15. The method according to claim 14 in which the promotor solvent is an alcohol.

55 16. The method according to any of claims 12 to 15, further comprising the presence of a monofunctional acrylate or methacrylate in the reacting mixture to stop the reaction and to extend the shelf life of the resultant acryl functional silicone.

17. The method according to any of claims 12 to 16, further comprising a free radical scavenger.

EP 0 230 342 B1

18. The method in accordance with any of claims 12 to 17, further comprising adding to the resultant product an acid anhydride which reacts with available =NH groups in the acryl functional silicone compound to produce the following group



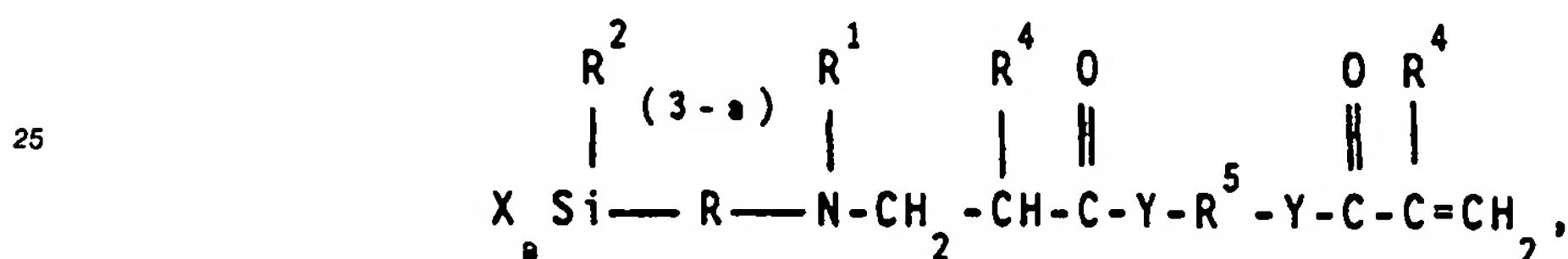
- wherein R^7 is a monovalent hydrocarbon radical or a radical of the general formula $-\text{R}^8\text{COOH}$ in which R^8 is a divalent hydrocarbon radical.

19. The acryl functional silicone compound according to claim 1 or 3 further comprising a photoinitiator which causes the acryl functional silicone compound to crosslink upon exposure to ultraviolet radiation.

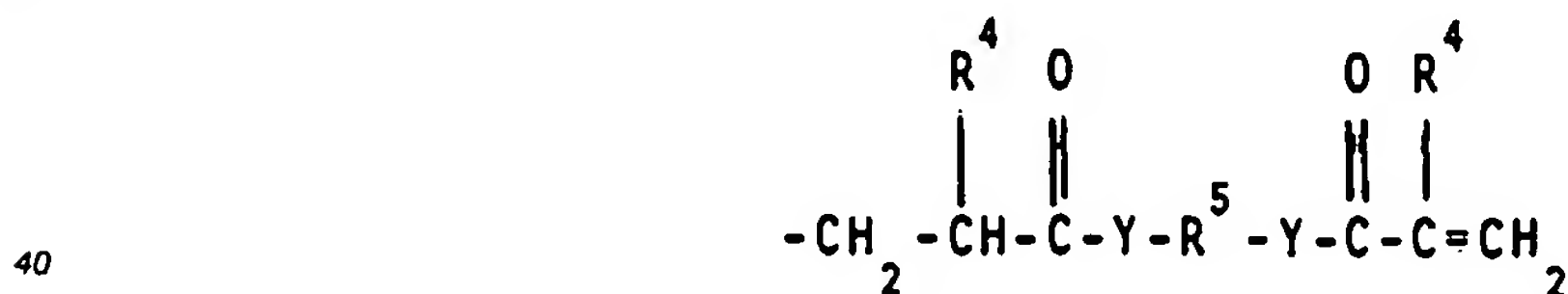
20. The acryl functional silicone compound according to claim 19 further comprising a storage stabilizer.

Patentansprüche

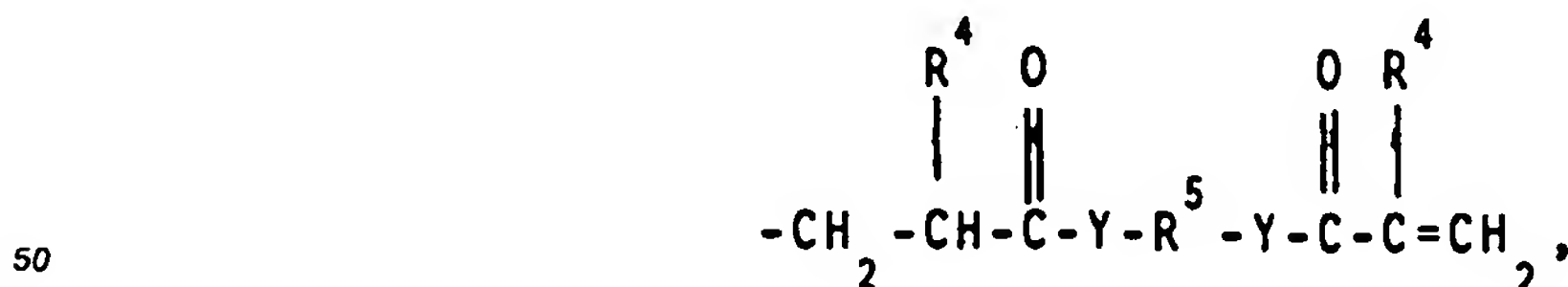
1. Acrylfunktionelle Siliconverbindung, in der die Verbindung ein Silan der nachfolgenden Formel ist



- in der R bedeutet: eine zweiwertige Kohlenwasserstoffgruppe, eine zweiwertige Kohlenwasserstoffgruppe mit Aminofunktionalität der Formel $=\text{NH}$, in der die zwei Bindungen des $=\text{NH}$ an Kohlenstoffatome gebunden sind, oder eine zweiwertige Kohlenwasserstoffgruppe mit Aminofunktionalität der Formel $=\text{NH}$, in der die zwei Bindungen des $=\text{NH}$ an Kohlenstoffatome gebunden sind und in denen der Wasserstoff des $=\text{NH}$ durch eine acrylfunktionelle Gruppe der allgemeinen Formel



ersetzt ist, wobei R^1 Wasserstoff, eine Alkylgruppe mit 1-4 Kohlenstoffatomen pro Gruppe oder eine acrylfunktionelle Gruppe der allgemeinen Formel ist



- R^2 ist eine einwertige Kohlenwasserstoffgruppe oder eine fluorierte Alkylgruppe,
X ist eine hydrolysierbare Gruppe, deren hydrolysierte Gruppen keine Stickstoffatome enthaltende Salze bilden,

R^4 ist ein Wasserstoffatom oder eine Methylgruppe,

R^5 ist eine zweiwertige Kohlenwasserstoffgruppe oder eine Etherbindungen enthaltende zweiwertige Kohlenwasserstoffgruppe.

EP 0 230 342 B1

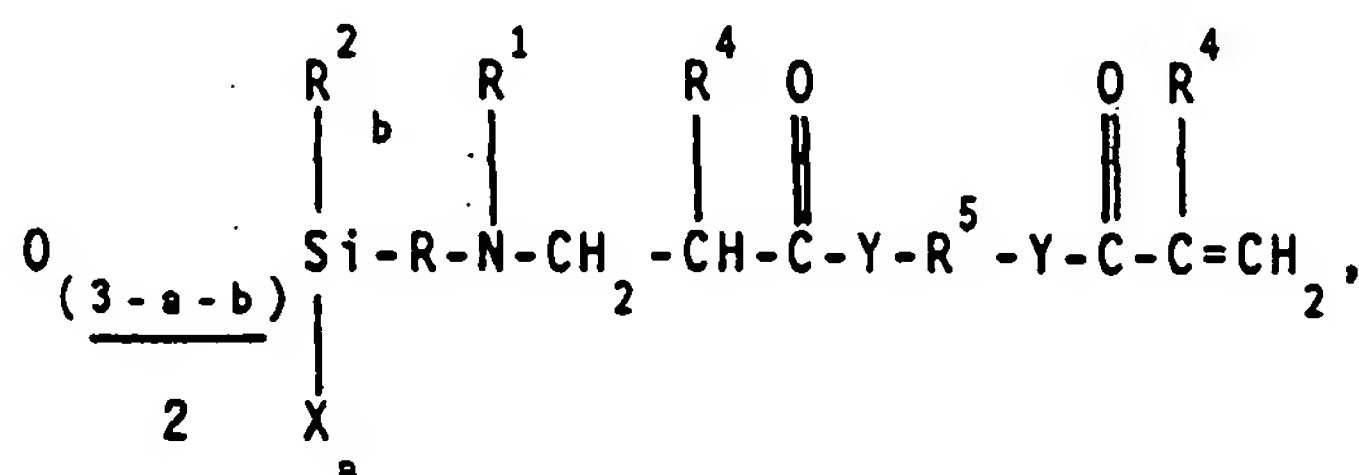
Y ist ein zweiwertiges Sauerstoffatom oder -NR¹-,
a ist 1, 2 oder 3.

2. Acrylfunktionelle Siliconverbindung nach Anspruch 1,

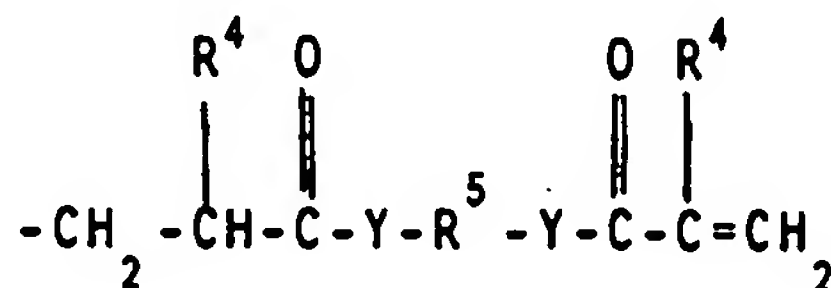
dadurch gekennzeichnet,

daß R eine Alkylengruppe mit 3-10 Kohlenstoffatomen pro Gruppe ist, R² Methyl ist, X OR³ ist, in der R³ eine Alkylgruppe mit 1-8 Kohlenstoffatomen pro Gruppe oder Phenyl ist, R⁴ ein Wasserstoffatom ist, R⁵ eine zweiwertige Kohlenwasserstoffgruppe ist, Y ein zweiwertiges Sauerstoffatom ist und a 3 ist.

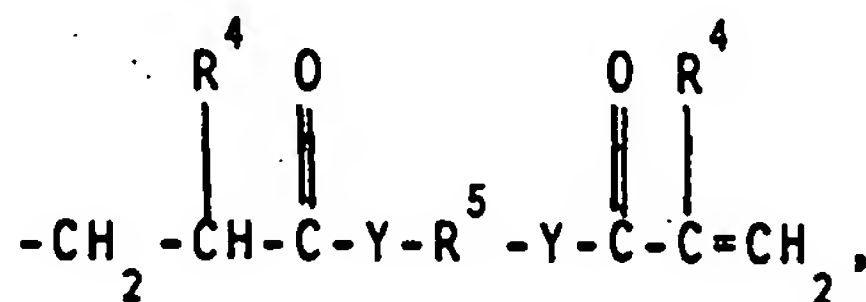
3. Acrylfunktionelle Siliconverbindung, in der die Verbindung ein Polysiloxan ist mit mindestens einer acrylfunktionellen Siloxaneinheit der allgemeinen Formel für die Einheit



in der R bedeutet: eine zweiwertige Kohlenwasserstoffgruppe, eine zweiwertige Kohlenwasserstoffgruppe mit Aminofunktionalität der Formel =NH, in der die zwei Bindungen des =NH an Kohlenstoffatome gebunden sind, oder eine zweiwertige Kohlenwasserstoffgruppe mit Aminofunktionalität der Formel =NH, in der die zwei Bindungen des =NH an Kohlenstoffatome gebunden sind und in denen der Wasserstoff des =NH durch eine acrylfunktionelle Gruppe der allgemeinen Formel



ersetzt ist, wobei R¹ eine Alkylgruppe mit 1-4 Kohlenstoffatomen pro Gruppe, eine acrylfunktionelle Gruppe der allgemeinen Formel ist



R² ist eine einwertige Kohlenwasserstoffgruppe oder eine fluorierte Alkylgruppe,

X ist eine hydrolysierbare Gruppe, deren hydrolysierte Gruppen keine Stickstoffatome enthaltende Salze bilden,

R⁴ ist ein Wasserstoffatom oder eine Methylgruppe,

R⁵ ist eine zweiwertige Kohlenwasserstoffgruppe oder eine Etherbindungen enthaltende zweiwertige Kohlenwasserstoffgruppe,

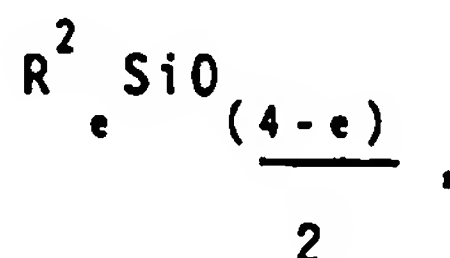
Y ist ein zweiwertiges Sauerstoffatom oder -NR¹-,

a ist 0, 1 oder 2,

b ist 0, 1 oder 2 und

a + b ist zwei oder kleiner und alle verbleibenden Siloxaneinheiten, die in dem Polysiloxan vorhanden sind, die allgemeine Formel der Einheit aufweisen

EP 0 230 342 B1

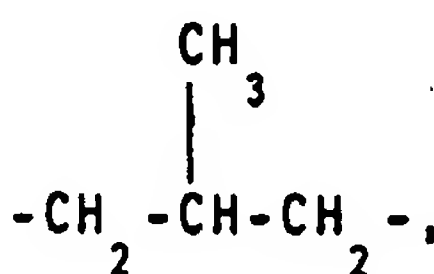


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in der R² die zuvor angegebene Bedeutung hat und e 0, 1, 2 oder 3 ist.

- 10 4. Polysiloxan nach Anspruch 3,
dadurch gekennzeichnet,
daß zwei acrylfunktionelle Siloxaneinheiten pro Molekül vorhanden sind, wobei a 0 ist, b 2 ist, R² Methyl
ist, R ist

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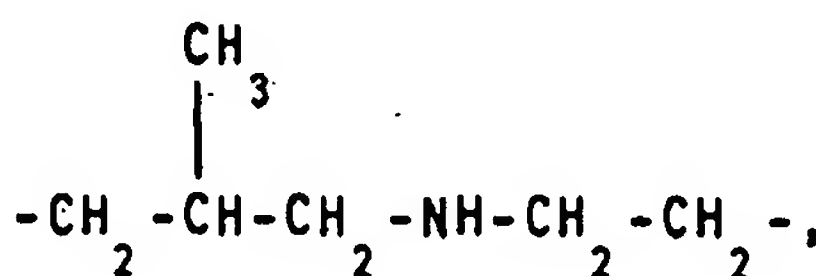
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R¹ Methyl ist, R⁴ ein Wasserstoffatom ist, Y ein zweiwertiges Sauerstoffatom ist, R⁵ eine zweiwertige Kohlenwasserstoffgruppe oder allgemeinen Formel -(CH₂)_d- ist, in der d eine ganze Zahl von 1-6 ist und wobei im Mittel von 10-300 Dimethylsiloxaneinheiten pro Molekül vorhanden sind.

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5. Polysiloxan nach Anspruch 3,
dadurch gekennzeichnet,
daß 2-20 acrylfunktionelle Siloxaneinheiten pro Molekül vorhanden sind, wobei a 0 ist, b 1 ist, R² Methyl
ist, R ist

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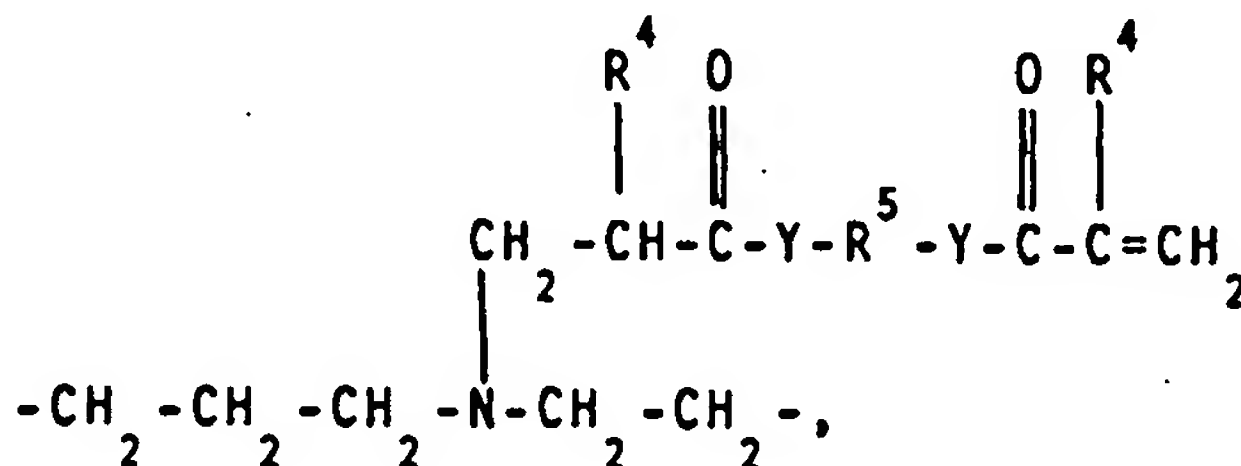
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R⁴ ein Wasserstoffatom ist, Y ein zweiwertiges Sauerstoffatom ist, R⁵ eine zweiwertige Kohlenwasserstoffgruppe der allgemeinen Formel -(CH₂)_d- ist, in der d eine ganze Zahl von 1-6 ist, wobei zwei Trimethylsiloxeinheiten pro Molekül und im Mittel von 100-500 Dimethylsiloxaneinheiten pro Molekül vorhanden sind.

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6. Polysiloxan nach Anspruch 3,
dadurch gekennzeichnet,
daß zwei acrylfunktionelle Siloxaneinheiten pro Molekül vorhanden sind, wobei a 0 ist, b 2 ist, R² Methyl
ist, R ist

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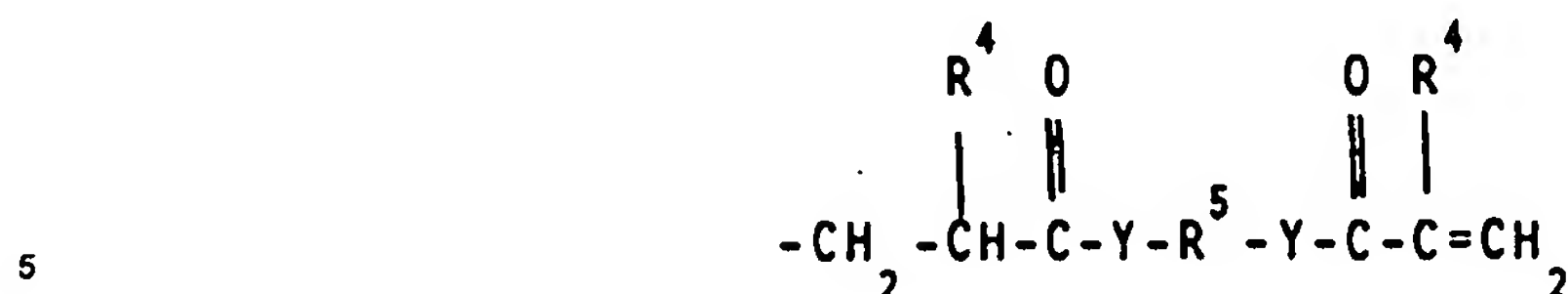


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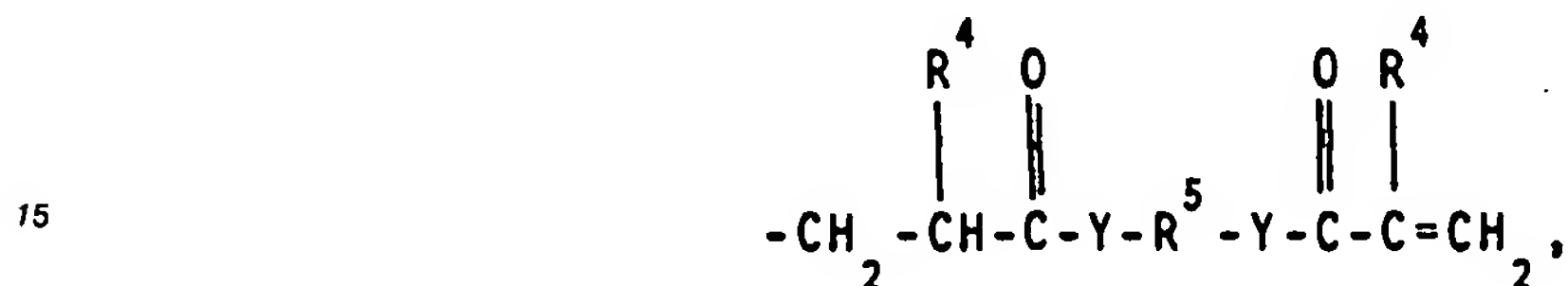
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R¹ Methyl ist, R⁴ ein Wasserstoffatom ist, Y ein zweiwertiges Sauerstoffatom ist, R⁵ eine zweiwertige

EP 0 230 342 B1



ersetzt ist, wobei R¹ Wasserstoff, eine Alkylgruppe mit 1-4 Kohlenstoffatomen pro Gruppe oder eine acrylfunktionelle Gruppe der allgemeinen Formel ist

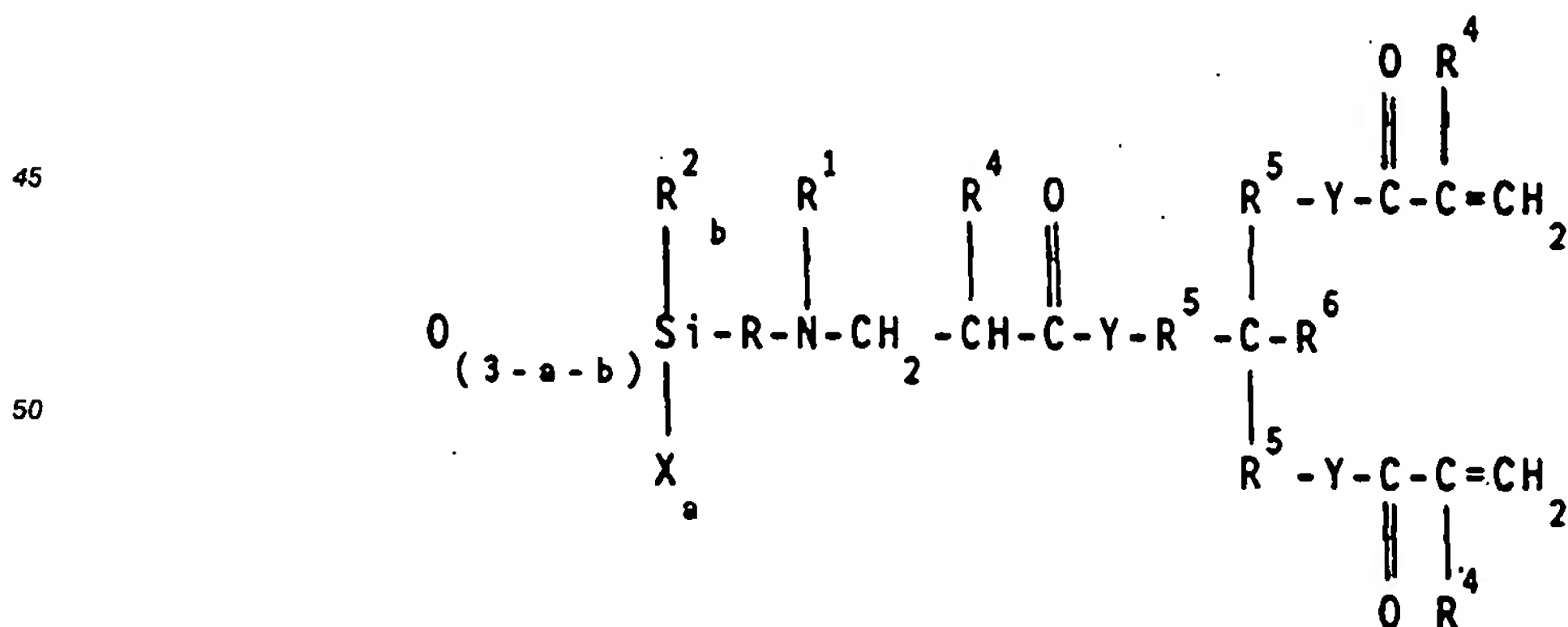


- 20 R² ist eine einwertige Kohlenwasserstoffgruppe oder eine fluorierte Alkylgruppe,
 X ist eine hydrolysierbare Gruppe, deren hydrolysierte Gruppen keine Stickstoffatome enthaltende Salze bilden,
 R⁴ ist ein Wasserstoffatom oder eine Methylgruppe,
 R⁵ ist eine zweiwertige Kohlenwasserstoffgruppe oder eine Etherbindungen enthaltende zweiwertige Kohlenwasserstoffgruppe,
 25 R⁶ ist ein einwertiger Rest, ausgewählt aus der Gruppe, bestehend aus einem Kohlenwasserstoffrest, einem mit Hydroxyl substituiertem, aliphatischen Kohlenwasserstoffrest und einer Acrylgruppe der Formel



35 Y ist ein zweiwertiges Sauerstoffatom oder -NR¹-,
 a ist 1, 2 oder 3.

- 40 10. Acrylfunktionelle Siliconverbindung, in der die Verbindung ein Siloxan ist mit mindestens einer Einheit der nachfolgenden allgemeinen Formel für die Einheit

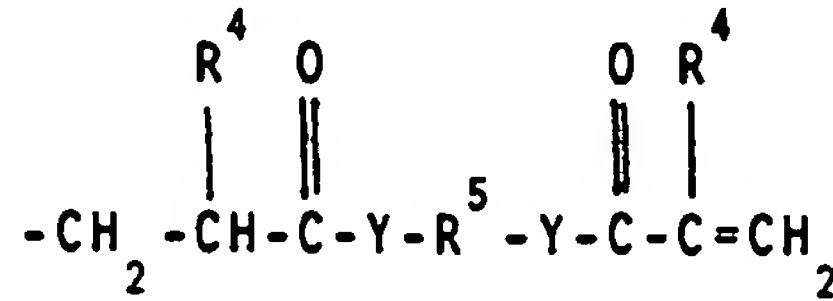


in der R bedeutet: eine zweiwertige Kohlenwasserstoffgruppe, eine zweiwertige Kohlenwasserstoffgruppe mit Aminofunktionalität der Formel =NH, in der die zwei Bindungen des =NH an Kohlenstoffatome

EP 0 230 342 B1

gebunden sind, oder eine zweiwertige Kohlenwasserstoffgruppe mit Aminofunktionalität der Formel =NH, in der die zwei Bindungen des =NH an Kohlenstoffatome gebunden sind und in denen der Wasserstoff des =NH durch eine acrylfunktionelle Gruppe der allgemeinen Formel

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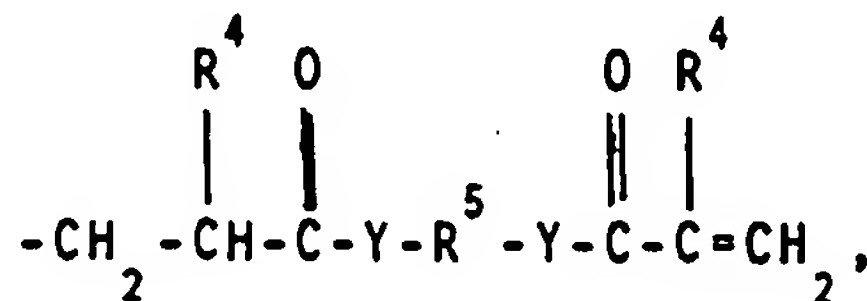


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ersetzt ist,

R¹ eine Alkylgruppe mit 1-4 Kohlenstoffatomen pro Gruppe oder eine acrylfunktionelle Gruppe der allgemeinen Formel ist

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R² ist eine einwertige Kohlenwasserstoffgruppe oder eine fluorierte Alkylgruppe,

X ist eine hydrolysierbare Gruppe, deren hydrolysierte Gruppen keine Stickstoffatome enthaltende Salze bilden,

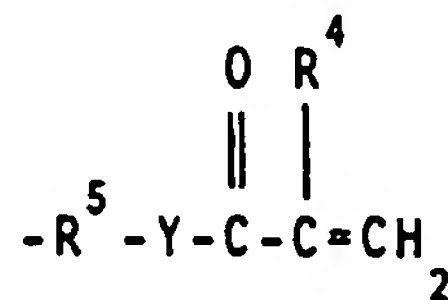
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R⁴ ist ein Wasserstoffatom oder eine Methylgruppe,

R⁵ ist eine zweiwertige Kohlenwasserstoffgruppe oder eine Etherbindungen enthaltende zweiwertige Kohlenwasserstoffgruppe,

R⁶ ist eine einwertige Gruppe, ausgewählt aus der Gruppe, bestehend aus einem Kohlenwasserstoffrest, einem mit Hydroxyl substituiertem, aliphatischen Kohlenwasserstoffrest und einer Acrylgruppe der Formel

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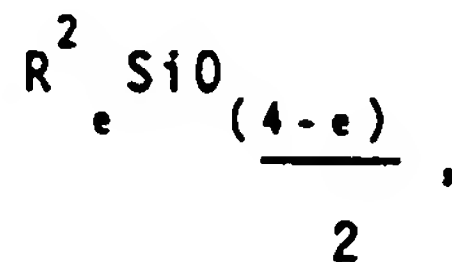
Y ist ein zweiwertiges Sauerstoffatom oder -NR¹-,

a ist 0, 1 oder 2,

b ist 0, 1 oder 2 und

a + b ist zwei oder kleiner und alle verbleibenden Siloxaneinheiten, die in dem Polysiloxan vorhanden sind, die allgemeine Formel der Einheit aufweisen

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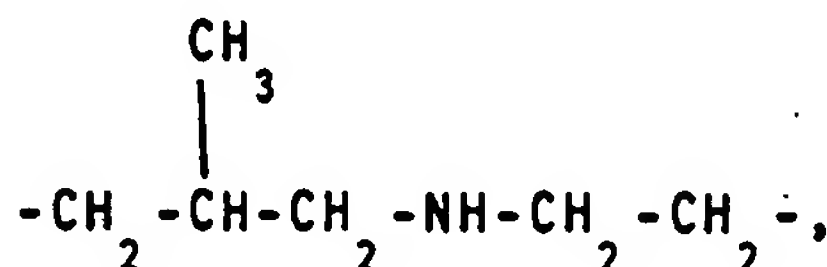
in der R² die zuvor angegebene Bedeutung hat und e 0, 1, 2 oder 3 ist.

55 11. Polysiloxan nach Anspruch 10,

dadurch gekennzeichnet,

daß 2-20 acrylfunktionelle Siloxaneinheiten vorhanden sind, in denen a 0 ist, b 1 ist, R ist

EP 0 230 342 B1



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10 R^4 ein Wasserstoffatom ist, Y ein zweiwertiges Sauerstoffatom ist, R^5 eine zweiwertige Kohlenwasserstoffgruppe der allgemeinen Formel $-(\text{CH}_2)_d-$ ist, in der d eine ganze Zahl von 1-6 ist und R^6 ist Ethyl, wobei zwei Trimethylsiloxyeinheiten pro Molekül und im Mittel von 100-500 Dimethylsiloxaneinheiten pro Molekül vorhanden sind.

12. Verfahren zum Herstellen einer acrylfunktionellen Siliconverbindung nach Ansprüchen 1-3 durch Ausbilden einer innigen Mischung einer aminofunktionellen Siliconverbindung, in der die Aminogruppe ein primäres oder sekundäres Amin ist, und einer acrylfunktionellen Verbindung mit mindestens zwei Acrylatgruppen, Methacrylatgruppen, Acrylamidgruppen oder Methacrylamidgruppen pro Molekül bei einer Temperatur unter 100°C für eine zum Herstellen einer acrylfunktionellen Siliconverbindung ausreichenden Zeit, wobei mindestens ein Siliziumatom eine über eine Silizium-Kohlenstoff-Bindung an das Siliziumatom gebundene acrylfunktionelle Gruppe aufweist, wobei die acrylfunktionelle Gruppe enthält mindestens eine Kohlenstoff-Stickstoff-Kohlenstoff-Bindung und eine Acrylatgruppe, Methacrylatgruppe, Acrylamidgruppe oder Methacrylamidgruppe, alle anderen an das Siliziumatom gebundenen Gruppen sind einwertige Kohlenwasserstoffgruppen, fluorierte Alkylgruppen, hydrolysierbare Gruppen, deren hydrolysierte Gruppen keine ein Stickstoffatom enthaltende Salze bilden, zweiwertige Sauerstoffatome, die zwei Siliziumatome in einer Si-O-Si-Bindung verbinden, zweiwertige Kohlenwasserstoffgruppen, die mindestens zwei Siliziumatome verbinden, und die vorhandenen Siliziumatome, die keine daran gebundene acrylfunktionelle Gruppe aufweisen, jede der anderen hier genannten Gruppen an sich gebunden aufweisen können.

13. Verfahren nach Anspruch 12,
dadurch gekennzeichnet,
daß die innige Mischung auf eine Temperatur über 25°C , jedoch nicht über 100°C , erwärmt wird.

14. Verfahren nach Anspruch 12 oder 13,
dadurch gekennzeichnet,
daß sie weiterhin ein unterstützendes Lösemittel in der Mischung enthält.

15. Verfahren nach Anspruch 14,
dadurch gekennzeichnet,
daß das unterstützende Lösemittel ein Alkohol ist.

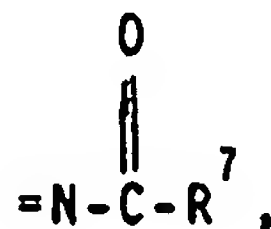
16. Verfahren nach jedem der Ansprüche 12-15,
dadurch gekennzeichnet,
daß weiterhin ein monofunktionelles Acrylat oder Methacrylat in der Reaktionsmischung vorhanden ist, um die Reaktion zu stoppen und die Lebensdauer des resultierenden acrylfunktionellen Silicons zu verlängern.

17. Verfahren nach jedem der Ansprüche 12-16,
dadurch gekennzeichnet,
daß weiterhin ein Fänger für freie Radikale vorhanden ist.

18. Verfahren nach jedem der Ansprüche 12-17,
dadurch gekennzeichnet,
daß dem resultierenden Produkt ein Säureanhydrid zugesetzt wird, das mit erhältlichlichen $=\text{NH}$ -Gruppen der acrylfunktionellen Siliconverbindung reagiert, um folgende Gruppe zu bilden

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EP 0 230 342 B1



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in der R^7 eine einwertige Kohlenwasserstoffgruppe oder eine Gruppe der allgemeinen Formel $-\text{R}^8\text{COOH}$ ist, in der R^8 eine zweiwertige Kohlenwasserstoffgruppe ist.

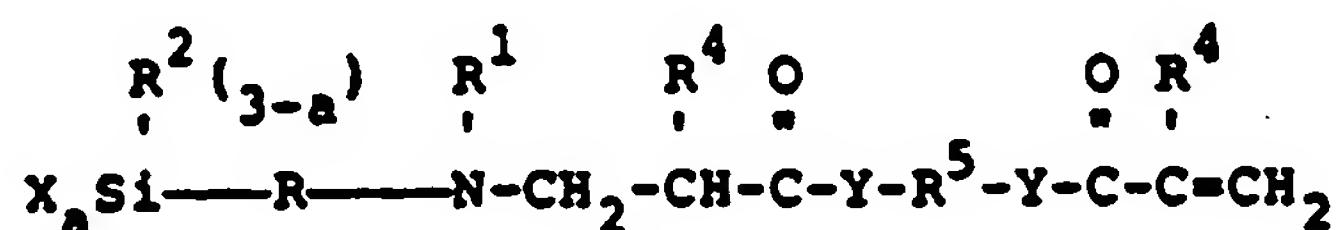
- 10 19. Acrylfunktionelle Siliconverbindung nach Anspruch 1 oder 3,
dadurch gekennzeichnet,
daß sie weiterhin einen Photoinitiator enthält, der bei Einwirkung von ultravioletter Strahlung die Vernetzung der acrylfunktionellen Siliconverbindung auslöst.
- 15 20. Acrylfunktionelle Siliconverbindung nach Anspruch 19,
dadurch gekennzeichnet,
daß sie weiterhin einen Lagerstabilisator enthält.

Revendications

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1. Un composé organosilicié à fonctionnalité acrylique, dans lequel le composé est un silane répondant à la formule suivante

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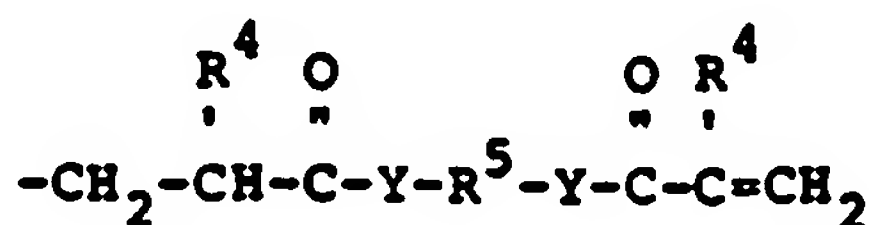
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dans laquelle

R est un radical hydrocarboné divalent, un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule $=\text{NH}$ où les deux liaisons de $=\text{NH}$ sont fixées à des atomes de carbone, ou un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule $=\text{NH}$ où les deux liaisons de $=\text{NH}$ sont fixées à des atomes de carbone et où l'hydrogène de $=\text{NH}$ est substitué par un groupe fonctionnel acrylique de la formule générale

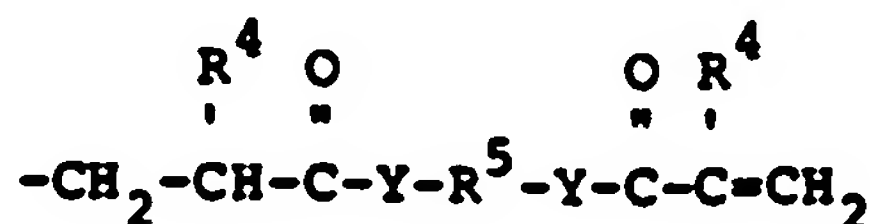
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R^1 est l'hydrogène, un radical alkyle ayant 1 à 4 atomes de carbone par radical, ou un radical fonctionnel acrylique de la formule générale

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R^2 est un radical hydrocarboné monovalent ou un radical alkyle fluoré,

X est un groupe hydrolysable dont les groupes hydrolysés ne forment pas de sels contenant un atome d'azote,

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R^4 est un atome d'hydrogène ou un radical méthyle,

R^5 est un radical hydrocarboné divalent ou un radical hydrocarboné divalent contenant des liaisons éther,

Y est un atome d'oxygène divalent ou $-\text{NR}^1-$,

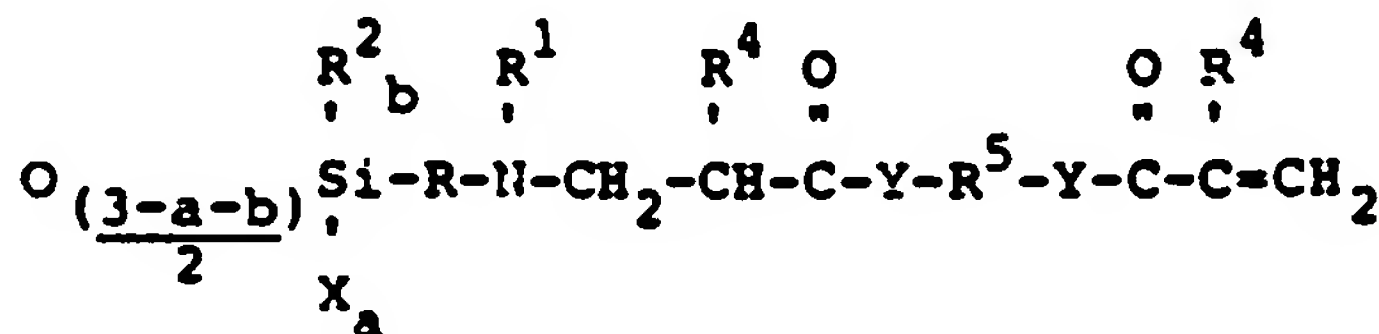
EP 0 230 342 B1

a est 1, 2 ou 3.

2. Le composé organosilicié à fonctionnalité acrylique selon la revendication 1, dans lequel R est un radical alkylène ayant 3 à 10 atomes de carbone par radical, R² est un radical méthyle, X est OR³ où R³ est un radical alkyle de 1 à 8 atomes de carbone par radical ou phényle, R⁴ est un atome d'hydrogène, R⁵ est un radical hydrocarboné divalent, Y est un atome d'oxygène divalent et a est 3.
3. Un composé organosilicié à fonctionnalité acrylique, dans lequel le composé est un polysiloxane ayant au moins un motif siloxane à fonctionnalité acrylique de la formule unitaire générale

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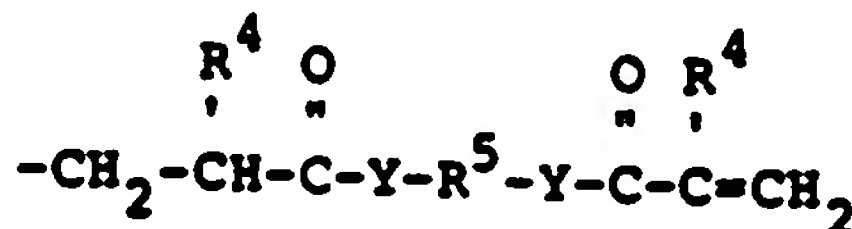
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dans laquelle

R est un radical hydrocarboné divalent, un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule =NH où les deux liaisons de =NH sont fixées à des atomes de carbone, ou un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule =NH où les deux liaisons de =NH sont fixées à des atomes de carbone et où l'hydrogène de =NH est substitué par un groupe fonctionnel acrylique de la formule générale

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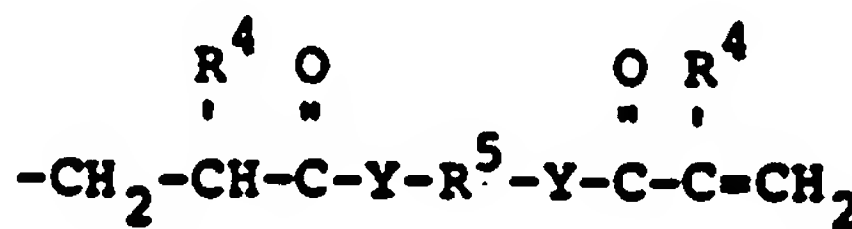
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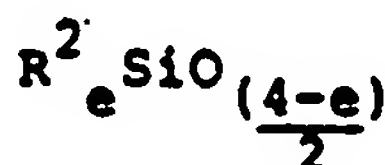
R¹ est un radical alkyle ayant 1 à 4 atomes de carbone par radical, un radical fonctionnel acrylique de la formule générale

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R² est un radical hydrocarboné monovalent ou un radical alkyle fluoré,
X est un groupe hydrolysable dont les groupes hydrolysés ne forment pas de sels contenant un atome d'azote,
R⁴ est un atome d'hydrogène ou un radical méthyle,
R⁵ est un radical hydrocarboné divalent ou un radical hydrocarboné divalent contenant des liaisons éther,
Y est un atome d'oxygène divalent ou -NR¹-,
a est 0, 1 ou 2,
b est 0, 1 ou 2, et
a + b vaut deux ou moins, et tous les motifs siloxanes restants éventuels présents dans le polysiloxane sont ceux de la formule unitaire générale

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dans laquelle R² est tel que défini ci-dessus et e est 0, 1, 2 ou 3.

EP 0 230 342 B1

4. Le polysiloxane selon la revendication 3, dans lequel il y a deux motifs siloxanes à fonctionnalité acrylique par molécule dans lesquels a est 0, b est 2, R² est un radical méthyle, R est



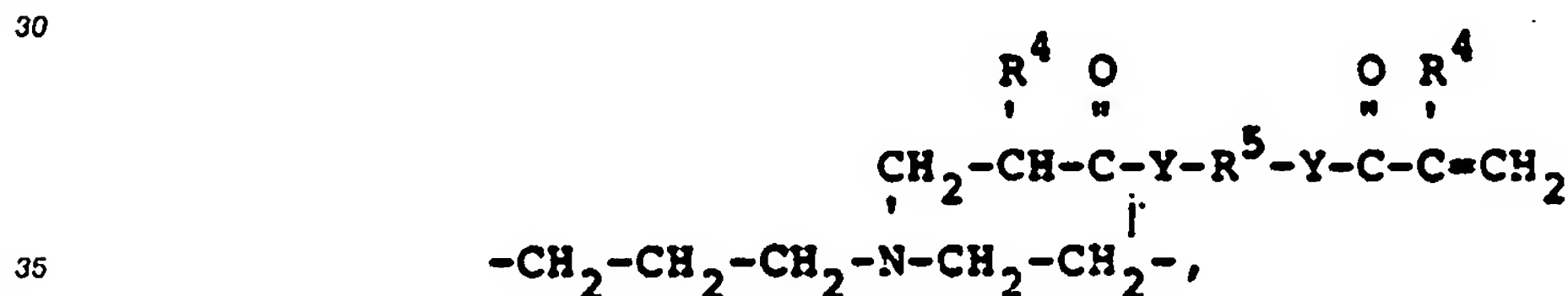
- 10 R¹ est un radical méthyle, R⁴ est un atome d'hydrogène, Y est un atome d'oxygène divalent, R⁵ est un radical hydrocarboné divalent de la formule générale -(CH₂)_d- où d est un nombre entier de 1 à 6 et il y a en moyenne 10 à 300 motifs diméthylsiloxane par molécule.

- 15 5. Le polysiloxane selon la revendication 3, dans lequel il y a 2 à 20 motifs siloxanes à fonctionnalité acrylique par molécule dans lesquels a est 0, b est 1, R² est un radical méthyle, R est



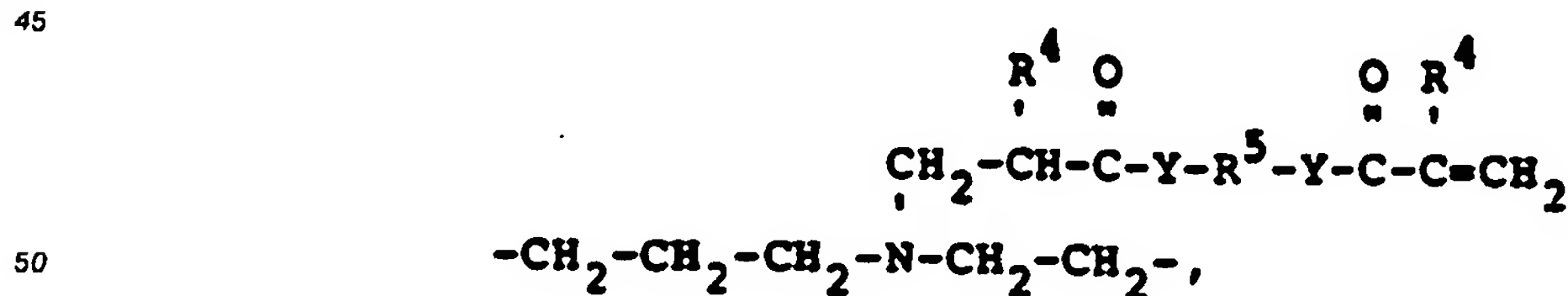
- 25 R⁴ est un atome d'hydrogène, Y est un atome d'oxygène divalent, R⁵ est un radical hydrocarboné divalent de la formule générale -(CH₂)_d- où d est un nombre entier de 1 à 6, il y a deux motifs triméthylsiloxyle par molécule, et il y a en moyenne 100 à 500 motifs diméthylsiloxane par molécule.

6. Le polysiloxane selon la revendication 3, dans lequel il y a deux motifs siloxanes à fonctionnalité acrylique par molécule dans lesquels a est 0, b est 2, R² est un radical méthyle, R est



- 40 R¹ est un radical méthyle, R⁴ est un atome d'hydrogène, Y est un atome d'oxygène divalent, R⁵ est un radical hydrocarboné divalent de la formule générale -(CH₂)_d- où d est un nombre entier de 1 à 6 et il y a en moyenne 10 à 300 motifs diméthylsiloxane par molécule.

7. Le polysiloxane selon la revendication 3, dans lequel il y a 2 à 20 motifs siloxanes à fonctionnalité acrylique par molécule dans lesquels a est 0, b est 1, R² est un radical méthyle, R est



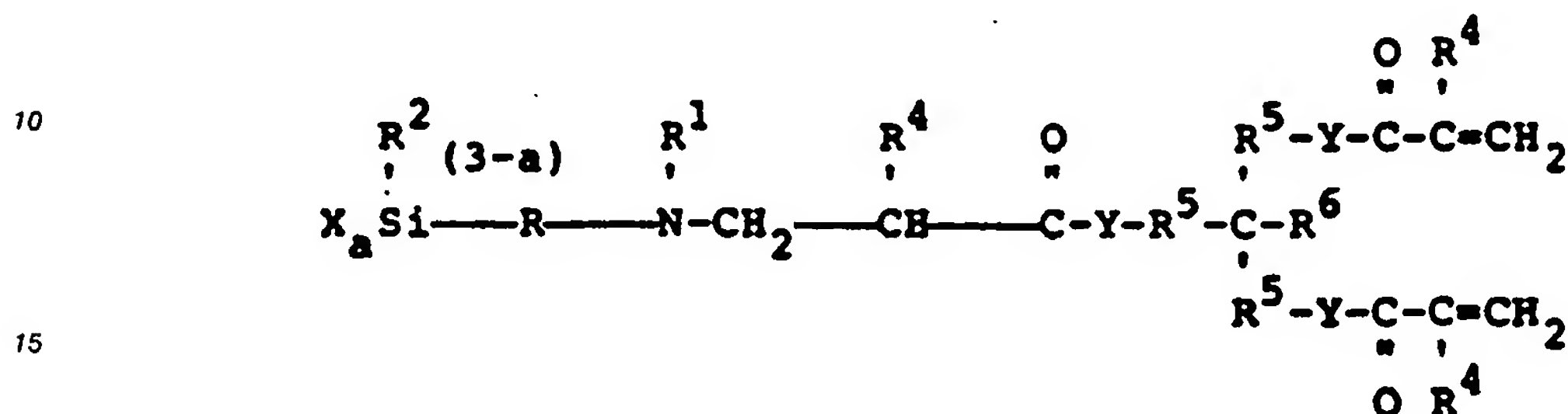
- 55 R⁴ est un atome d'hydrogène, Y est un atome d'oxygène divalent, R⁵ est un radical hydrocarboné divalent de la formule générale -(CH₂)_d- où d est un nombre entier de 1 à 6, il y a deux motifs triméthylsiloxyle par molécule, et il y a en moyenne 100 à 500 motifs diméthylsiloxane par molécule.

8. Le polysiloxane selon la revendication 3, dans lequel il y a deux motifs siloxanes à fonctionnalité acrylique par molécule dans lesquels a est 0, b est 2, R² est un radical méthyle, R est -CH₂-CH₂-CH₂-,

EP 0 230 342 B1

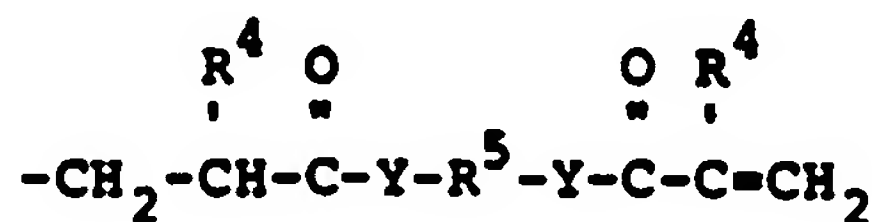
R¹ est un radical méthyle, R⁴ est un atome d'hydrogène, Y est un atome d'oxygène divalent, R⁵ est un radical hydrocarboné divalent de la formule générale -(CH₂)_d- où d est un nombre entier de 1 à 6 et il y a en moyenne 10 à 300 motifs diméthylsiloxane par molécule.

- 5 9. Un composé organosilicié à fonctionnalité acrylique, dans lequel le composé est un silane répondant à la formule générale suivante

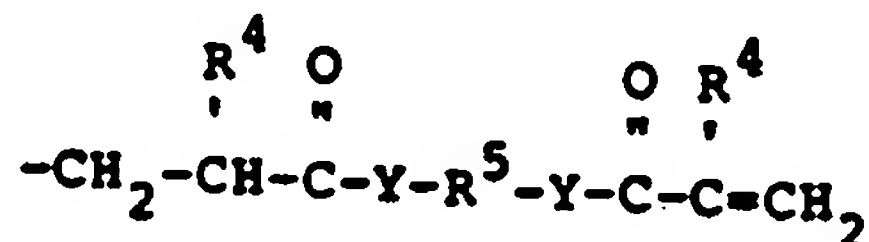


dans laquelle

R est un radical hydrocarboné divalent, un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule =NH où les deux liaisons de =NH sont fixées à des atomes de carbone, ou un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule =NH où les deux liaisons de =NH sont fixées à des atomes de carbone et où l'hydrogène de =NH est substitué par un groupe fonctionnel acrylique de la formule générale



R¹ est l'hydrogène, un radical alkyle ayant 1 à 4 atomes de carbone par radical, ou un radical fonctionnel acrylique de la formule générale



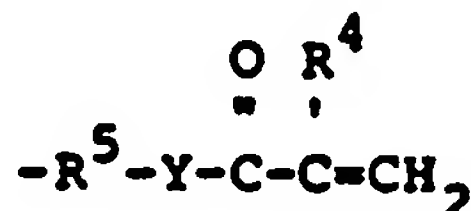
R² est un radical hydrocarboné monovalent ou un radical alkyle fluoré,

X est un groupe hydrolysable dont les groupes hydrolysés ne forment pas de sels contenant un atome d'azote,

R⁴ est un atome d'hydrogène ou un radical méthyle,

R⁵ est un radical hydrocarboné divalent ou un radical hydrocarboné divalent contenant des liaisons éther,

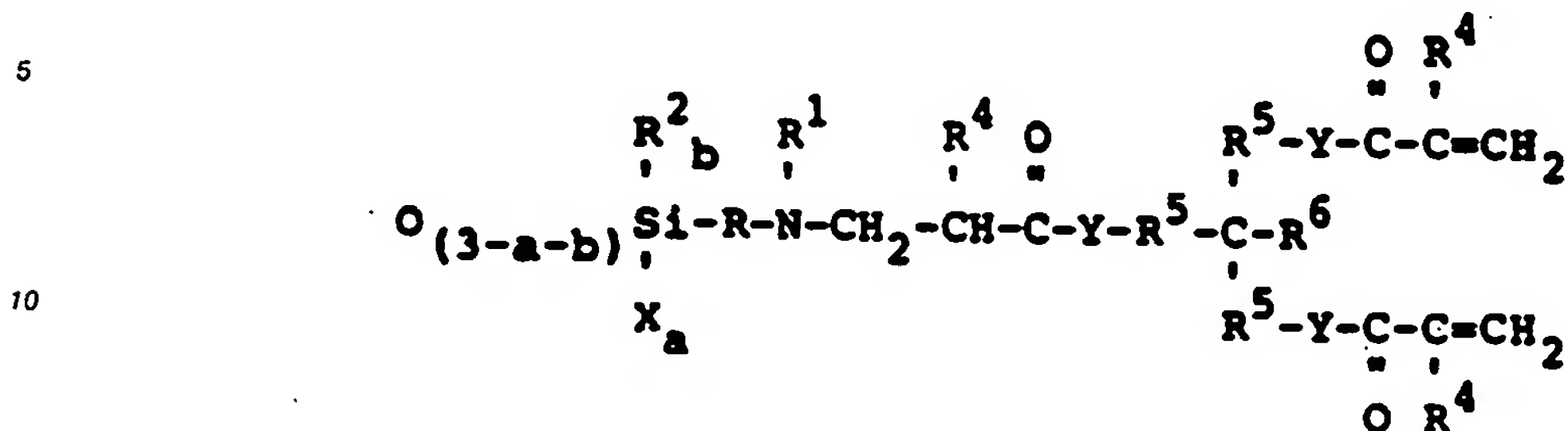
R⁶ est un radical monovalent choisi dans le groupe formé par un radical hydrocarboné, un radical hydrocarboné aliphatique à substituant hydroxyle et un radical acrylique de la formule



Y est un atome d'oxygène divalent ou -NR¹-,
a est 1, 2 ou 3.

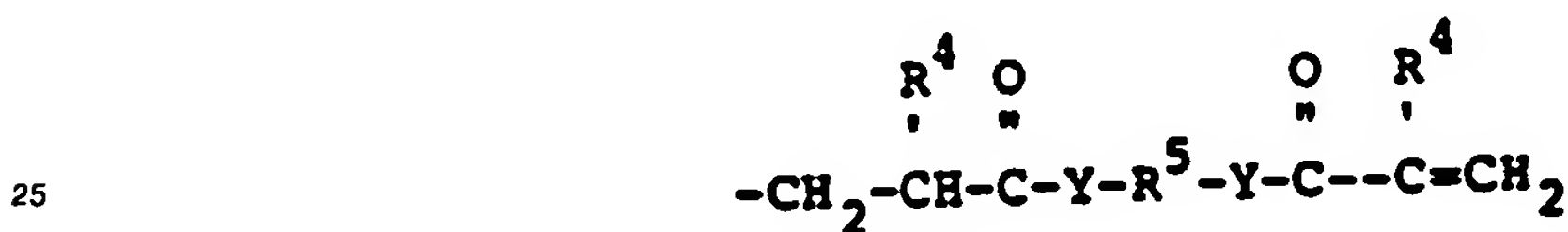
EP 0 230 342 B1

10. Un composé organosilicié à fonctionnalité acrylique, dans lequel le composé est un siloxane ayant au moins un motif de la formule unitaire générale suivante

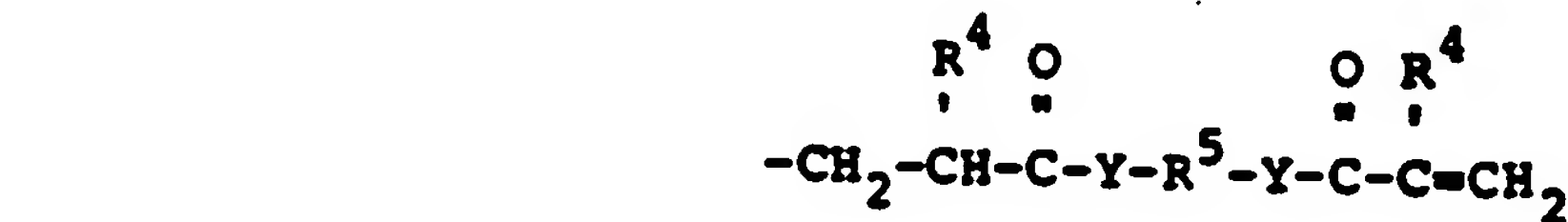


dans laquelle

R est un radical hydrocarboné divalent, un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule =NH où les deux liaisons de =NH sont fixées à des atomes de carbone, ou un radical hydrocarboné divalent ayant une fonctionnalité amino de la formule =NH où les deux liaisons de =NH sont fixées à des atomes de carbone et où l'hydrogène de =NH est substitué par un groupe fonctionnel acrylique de la formule générale



R¹ est un radical alkyle ayant 1 à 4 atomes de carbone par radical, ou un radical fonctionnel acrylique de la formule générale



R² est un radical hydrocarboné monovalent ou un radical alkyle fluoré,

X est un groupe hydrolysable dont les groupes hydrolysés ne forment pas de sels contenant un atome d'azote,

R⁴ est un atome d'hydrogène ou un radical méthyle,

R⁵ est un radical hydrocarboné divalent ou un radical hydrocarboné divalent contenant des liaisons éther,

R⁶ est un radical monovalent choisi dans le groupe formé par un radical hydrocarboné, un radical hydrocarboné aliphatique à substituant hydroxyle, et un radical acrylique de la formule



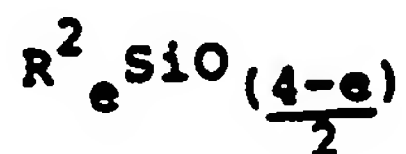
Y est un atome d'oxygène divalent ou -NR¹-,

a est 0, 1 ou 2,

b est 0, 1 ou 2, et

a + b vaut deux ou moins, et tous les motifs siloxanes restants éventuels présents dans le polysiloxane sont ceux de la formule unitaire générale

EP 0 230 342 B1

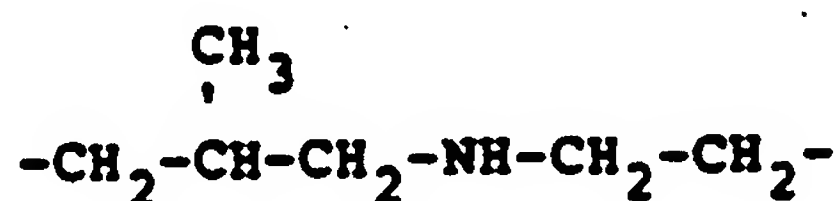


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dans laquelle R^2 est tel que défini ci-dessus et e est 0, 1, 2 ou 3.

11. Le polysiloxane selon la revendication 10, dans lequel il y a 2 à 20 motifs siloxanes à fonctionnalité acrylique dans lesquels a est 0, b est 1, R est

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R^4 est un atome d'hydrogène, Y est un atome d'oxygène divalent, R^5 est un radical hydrocarboné divalent de la formule générale $-(CH_2)_d-$ où d est un nombre entier de 1 à 6, et R^6 est un radical éthyle, il y a deux motifs triméthylsiloxyle par molécule, et il y a en moyenne 100 à 500 motifs diméthylsiloxane par molécule.

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12. Un procédé de préparation d'un composé organosilicié à fonctionnalité acrylique tel que revendiqué dans la revendication 1 ou 3, consistant à former un mélange intime d'un composé du silicium à fonctionnalité amino dans lequel le groupe amino est une amine primaire ou une amine secondaire et d'un composé à fonctionnalité acrylique ayant au moins deux groupes acrylate, méthacrylate, acrylamide ou méthacrylamide par molécule, à une température inférieure à 100°C pendant une durée suffisante pour produire un composé organosilicié à fonctionnalité acrylique dans lequel au moins un atome de silicium porte un radical fonctionnel acrylique lié au silicium par une liaison silicium-carbone, où le radical fonctionnel acrylique contient au moins une liaison carbone-azote-carbone et un groupe acrylate, méthacrylate, acrylamide ou méthacrylamide, tous les autres groupes éventuels liés à l'atome de silicium étant des radicaux hydrocarbonés monovalents, des radicaux alkyles fluorés, des groupes hydrolysables dont les groupes hydrolysés ne forment pas de sel contenant un atome d'azote, des atomes d'oxygène divalents qui relient deux atomes de silicium dans une liaison Si-O-Si, des radicaux hydrocarbonés divalents reliant au moins deux atomes de silicium ensemble, et les atomes de silicium qui sont présents et qui ne portent pas de radical fonctionnel acrylique lié à eux peuvent porter, liés à eux, n'importe lesquels des autres groupes tels que mentionnés ici.

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13. Le procédé selon la revendication 12, dans lequel le mélange intime est chauffé à une température supérieure à 25°C mais ne dépassant pas 100°C.

14. Le procédé selon la revendication 12 ou 13, comprenant de plus un solvant d'activation dans le mélange.

15. Le procédé selon la revendication 14, dans lequel le solvant d'activation est un alcool.

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16. Le procédé selon l'une quelconque des revendications 12 à 15, comprenant de plus la présence d'un acrylate ou méthacrylate monofonctionnel dans le mélange réagissant pour arrêter la réaction et pour prolonger la durée de conservation au stockage du composé organosilicié à fonctionnalité acrylique résultant.

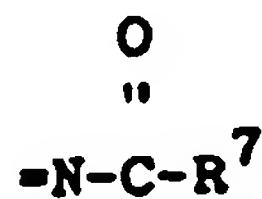
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17. Le procédé selon l'une quelconque des revendications 12 à 16, comprenant de plus un agent éliminateur de radicaux libres.

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18. Le procédé selon l'une quelconque des revendications 12 à 17, consistant de plus à ajouter au produit résultant un anhydride d'acide qui réagit avec les groupes =NH disponibles dans le composé organosilicié à fonctionnalité acrylique pour produire le groupe suivant

EP 0 230 342 B1



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où R⁷ est un radical hydrocarboné monovalent ou un radical de la formule générale -R⁸COOH où R⁸ est un radical hydrocarboné divalent.

10 19. Le composé organosilicié à fonctionnalité acrylique selon la revendication 1 ou 3, comprenant de plus un photo-initiateur qui provoque la réticulation du composé organosilicié à fonctionnalité acrylique lors de son exposition à un rayonnement ultraviolet.

15 20. Le composé organosilicié à fonctionnalité acrylique selon la revendication 19, comprenant de plus un stabilisant au stockage.

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